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METHODS OF CHEMICAL ANALYSIS OF FERRO-ALLOYS

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
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Indian Standard
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Indian Standard

METHODS OF CHEMICAL ANALYSIS OF FERRO-ALLOYS

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 16 September 1961, after the draft finalized by the Methods of Chemical Analysis Sectional Committee had been approved by the Structural and Metals Division Council.

0.2 The ferro-alloy industry is growing fast and although the well established iron and steel industry has been using ferro-alloys for nearly 50 years, the various laboratories have been following different methods for the chemical analysis of these alloys. As the results reported are not always in agreement, the necessity for prescribing standard methods is obvious.

0.3 In preparing this standard, due consideration has been given to the existing practices and facilities available in this country for such analysis, as these methods are to be used as reference methods in case of disputes.

0.4 Taking into consideration the views of producers, consumers and testing authorities, it was felt that it should be related to the technological methods followed in the country in this field. Furthermore, due weightage had to be given to the need for international co-ordination among standards prevailing in different countries of the world in this field. These considerations led the Sectional Committee to derive assistance from the following standards and publications:

B. S. 1121 METHODS FOR THE ANALYSIS OF IRON AND STEEL. British Standards Institution.

PIGGOT, E. C., Ferrous Analysis — Modern Practice and Theory, 2nd Edition, London, Chapman & Hall, 1954.

ASTM METHODS FOR CHEMICAL ANALYSIS OF METALS 1956. American Society for Testing Materials.

FURMAN, N. H. (Ed)., SCOTT W. W., Standard Methods of Chemical Analysis, 5th Edition, New York. D Van Nostrand Company Inc., 1948.

LUNDELL, G. E. F., HOFFMAN, J. I., And BRIGHT, M. A., Chemical Analysis of Iron & Steel, 4th Printing. New York. John Wiley & Sons, 1946.

0.5 Wherever a reference to any Indian Standard appears in this standard, it shall be taken as a reference to the latest verison of the standard.

0.6 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960 Rules for Rounding Off Numerical Values (*Revised*).

1. SCOPE

1.1 This standard prescribes in nine sections the analysis of ferrosilicon, ferrochromium, ferromanganese and speigeleisen, silicomanganese, ferromolybdenum, ferrophosphorus, ferrotitanium, ferrovanadium and ferrotungsten. The methods have been prescribed to cover the composition ranges as given in Appendix A.

2. SAMPLING

2.1 Samples shall be drawn and prepared in accordance with the procedures laid down under IS : 1472(Part I)-1959 Methods of Sampling Ferro-Alloys,(Part I).

3. QUALITY OF REAGENTS

3.1 Unless specified otherwise, pure chemicals and distilled water [*see* IS : 1070-1960 Water, Distilled Quality (*Revised*)] shall be used.

Note — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4. GENERAL

4.1 Use of Filter Papers — In the methods prescribed in this standard, only relative numbers of Whatman filter paper have been prescribed, since the latter are commonly used. However, any other suitable brand of filter papers with equivalent porosity may also be used.

SECTION I FERROSILICON

5. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

5.1 Outline of the Method — The sample is decomposed by sodium hydroxide fusion, and complete dehydration of silica affected by double evaporation of the acidified extract. Silica is then determined by hydrofluorization.

5.2 Apparatus

5.2.1 *Nickel Crucible* — 30 to 50 ml capacity, with lid.

5.2.2 *Platinum Crucible* — 25 to 30 ml capacity, with lid.

5.3 Reagents

5.3.1 *Sodium Hydroxide* — solid.

5.3.2 *Dilute Hydrochloric Acid* — 1 : 1 and 1 : 20 (*v/v*).

5.3.3 *Concentrated Hydrochloric Acid* — sp gr 1·16 (conforming to *IS : 265-1950 Specification for Hydrochloric Acid).

5.3.4 *Dilute Sulphuric Acid* — 1 : 1 (*v/v*).

5.3.5 *Hydrofluoric Acid* — 40 percent.

5.4 Procedure

5.4.1 Place 8 to 10 g of sodium hydroxide in the nickel crucible and transfer 0·25 to 0·5 g of the dried and powdered alloy ground to pass through IS Sieve 15, to the crucible depending upon the silicon content of the sample. Cover the crucible with the lid and heat, at first gently and then at the maximum heat for half an hour. Carefully fuse over a low flame, slowly revolving it round the outer edge of the flame till the contents have melted down without spattering. Rotate the crucible carefully to stir any unattacked particles in the bottom and sides, maintaining it at a low red heat. Just before completion of the fusion which requires 3 to 4 minutes, increase the temperature of the crucible to bright redness for one minute. Spread the melt uniformly on the sides and bottom of the crucible by slowly rotating it and allow to cool to room temperature.

5.4.2 Extract the melt with minimum quantity of hot water in a porcelain dish, washing the crucible and lid with a jet of hot water. Acidify carefully with dilute hydrochloric acid (1 : 1) and add about 50 ml excess. Evaporate to dryness and bake for one hour at 100 to 110°C. Redissolve the mass in 40 ml of concentrated hydrochloric acid by warming, and dilute with 150 ml of hot water. Raise to boil, allow to settle slightly and filter through filter paper No. 40. Wash 10 to 12 times alternately with hot dilute hydrochloric acid (1 : 20) and hot water. Finally rinse with hot water till the washings are free from chlorides. Preserve the paper and the residue.

5.4.3 Evaporate the filtrate and washings to dryness and repeat the procedure of baking, washing, etc, as given under **5.4.2**.

5.4.4 Place the papers and residue from **5.4.2** and **5.4.3** in the platinum crucible and dry completely on a hot-plate. Heat the crucible in a muffle furnace at 1 000°C for about 30 minutes, cool in a desiccator and weigh. Ignite again for 10 minutes at the above temperature as a check for constant weight.

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*Since revised.

5.4.5 Add sufficient dilute sulphuric acid to moisten the residue, then add carefully about 10 ml of hydrofluoric acid and cautiously evaporate to dryness. Ignite over a free flame to constant weight. Record the loss in weight which represents the weight of silica.

NOTE — A blank determination should be carried out when the silica content of the ferro-alloy is below 10 percent.

5.5 Calculation

$$\text{Silicon, percent} = \frac{A \times 46{\cdot}72}{B}$$

where

A = weight in g of silica obtained, and

B = weight in g of the sample taken.

6. DETERMINATION OF SILICON BY THE RAPID VOLUMETRIC (ALTERNATE) METHOD

6.1 Outline of the Method — This method is based on the reaction between silicic acid and potassium fluoride in acid solution which gives insoluble potassium fluosilicate. The latter is filtered, dissolved in hot water and titrated with standard sodium hydroxide solution.

6.2 Apparatus

6.2.1 *Plastic Beakers* — with plastic covers and plastic rods for stirring. The plastic material used shall be resistant to hydrofluoric acid.

6.3 Reagents

6.3.1 *Concentrated Nitric Acid* — sp gr 1·42 (conforming to *IS: 264-1950 Specification for Nitric Acid).

6.3.2 *Hydrofluoric Acid* — 40 percent.

6.3.3 *Potassium Chloride Solution* — 20 percent (*w/v*).

6.3.4 *Phenolphthalein Indicator Solution* — one percent (*w/v*) solution in alcohol.

6.3.5 *Standard Sodium Hydroxide Solution* — 0·25 N. The solution shall be standardized against succinic acid or potassium biphthalate.

6.4 Procedure — Weigh accurately 0·2 g of finely ground sample in a plastic beaker, add 30 ml of concentrated nitric acid and then 10 ml of hydrofluoric acid slowly in small amounts. Shake occasionally the plastic container to hasten the reaction. Control the temperature carefully during the reaction so that it is kept below 80°C. When a clear solution is obtained, give a few more shakings to the beaker to remove traces of nitrous fumes. Add 20 ml of water, rinse down the sides of the beaker and add 30 ml of potassium chloride solution with stirring. A little paper pulp may be added to facilitate the coagulation and settling of precipitate. Cool in ice for about half an hour and stir occasionally. Filter the precipitate through platinum Gooch crucible with paper pad; wash with 100 ml of potassium chloride solution until free of acid. Transfer the pad alongwith precipitate to an Erlenmeyer flask, add 50 ml of boiling water, washing down the sides of the Gooch crucible. Shake the flask to disintegrate the paper pad and bring to boil. Add 10 drops of phenolphthalein indicator solution and titrate against the standard sodium hydroxide solution.

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*Since revised.

6.5 Calculation

$$\text{Silicon, percent} = \frac{A \times 0{\cdot}175\,4}{B}$$

where

A = volume in ml of standard sodium hydroxide solution consumed by the test solution, and

B = weight in g of the sample taken.

7. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

7.1 Outline of the Method — The sample is burnt in a stream of pure oxygen, and the resulting carbon dioxide is absorbed in soda asbestos after removal of the contaminants. The increase in weight of the absorbent is proportional to the carbon content of the sample.

7.2 Apparatus — The assembly of apparatus is shown in Fig. 1.

7.2.1 *Source of Oxygen Supply* — gas holder *A* (capacity 8 to 10 litres) containing 99·5 percent oxygen, free from carbonaceous matter, connected by rubber tubing with the gas purifying train. The gas holder should be filled up before starting the operation.

7.2.2 *Oxygen Purification Train* — consists of Arnold bottles (*B*) and (*C*), the latter containing concentrated sulphuric acid, the exit bulb of which is packed with glass wool and another absorption bottle (*D*) containing soda asbestos which passes through IS Sieve 140 but is retained on IS Sieve 50 and 'anhydrone' in layers, connected in series between the gas holder and the inlet end of the combustion tube. A layer of about 12 mm of anhydrone is placed on top for removing

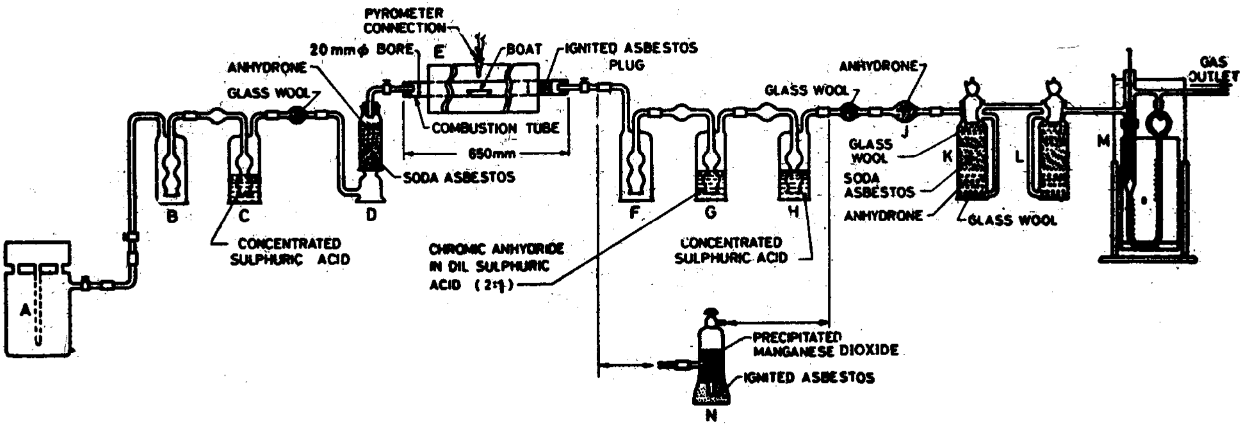

Fig. 1 Apparatus for Determination of Carbon (Total) by the Direct Combustion (Gravimetric) Method

moisture in the gas and the soda asbestos removes carbon dioxide in the gas. '

7.2.3 *Furnace* — a horizontal tube furnace (*E*) heated to 1 350°C by electricity.

7.2.4 *Combustion Tube* — A combustion tube approximately 650 mm long and of 20 mm inner diameter made of fused silica, fireclay or any other suitable material, should be used. In the exit end of the tube an ignited asbestos plug 75 mm long is placed lightly to retain ferric oxide carried over by the gas stream.

7.2.5 *Absorption Train* — consists of an Arnold bottle (*F*) to prevent back suction, a gas absorption bottle (*G*) filled with chromic anhydride in dilute sulphuric acid 2 : 1 (*v/v*) to remove oxides of sulphur from the gas stream, a bottle (*H*) containing about 40 ml of concentrated sulphuric acid to remove most of the moisture from exit gas, the exit end of this bottle is filled with glass wool to remove sulphuric acid mist, one tube (*J*) containing 'anhydrone' or any other suitable desiccant and carbon dioxide absorption bottle (*K*) (80 ml capacity) containing a layer of soda asbestos or ascarite, which should be uniformly graded and evenly packed with a layer of anhydrone on the top, all connected in series with the exit end of the combustion furnace and the atmosphere. The fillings in (*K*) are held in position by small plugs of glass wool. A bottle (*L*) packed similarly to bottle (*K*) acts as a guard against atmospheric gases. Its exit end is attached to a flowmeter. Bottles (*F*), (*G*) and (*H*) may be replaced by a Midvale or Nesbitt bulb (*N*) containing precipitated manganese dioxide over ignited asbestos.

7.3 Reagents

7.3.1 *Concentrated Sulphuric Acid* — sp gr 1·84 (conforming to*IS: 266-1950 Specification for Sulphuric Acid).

7.3.2 *Dilute Sulphuric Acid* — 2 : 98 (*v/v*).

7.3.3 *Chromic-Sulphuric Acid Solution* — Saturate 100 ml of dilute sulphuric acid (2 : 1) with chromic anhydride.

7.3.4 *Manganese Sulphate* — solid.

7.3.5 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

7.3.6 *Ammonium Persulphate Solution* — 25 and 22·5 percent (*w/v*).

7.3.7 *Precipitated Manganese Dioxide*

a) Dissolve 200 g of manganese sulphate ($MnSO_4$, $4H_2O$) in 2 500 ml of water, add concentrated ammonium hydroxide until ammoniacal, followed by 1 000 ml of freshly prepared ammonium persulphate solution (22·5 percent) and heat to boiling. Boil for 10 minutes, adding more of concentrated ammonium hydroxide to maintain the ammoniacal condition. Further addition of solutions of ammonium persulphate and ammonium hydroxide may be required until precipitation is judged to be complete.

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*Since revised.

b) Discontinue boiling and allow the precipitate to settle; wash by decantation 6 to 8 times with 500 to 600 ml portions of water, allowing the precipitate to settle completely between washings. Finally, wash 2 to 3 times by decantation with 500 to 600 ml portions of dilute sulphuric acid. Transfer the precipitate to a Buchner funnel and wash with hot water until free from sulphates. Dry the residue at 105 to 110°C, grind to pass IS Sieves 85 to 70 (aperture 842 to 708 microns) and again dry thoroughly at 105 to 110°C.

7.3.8 *Soda Asbestos* — It should be graded to IS Sieves 140 to 50 (aperture 1 405 to 500 microns).

7.3.9 *Anhydrone or Magnesium Perchlorate* $Mg(ClO_4)_2$ — The supply bottle should be well stoppered.

7.3.10 *Lead Foil* — This should be of assay grade and 0·127 mm in thickness.

7.3.11 *Magnesite Brick Powder* — Magnesite brick powder which has passed through IS Sieve 50 (aperture 500 microns) shall be used for spreading in the boat on which the sample is to be placed before combustion. This powder shall be calcined in the open muffle furnace prior to use, in order to eliminate any carbonaceous matter.

7.4 Procedure

7.4.1 Heat the furnace to a temperature between 1 250 and 1 350°C. Before starting the analysis, test the apparatus for any leaks. Pass a slow stream of oxygen for about 15 minutes through the whole train of the apparatus and then weigh the carbon dioxide absorption tube. A counterpoise of a similar bottle is recommended in a balance for weighing. After taking the first weight connect it back to the apparatus, pass oxygen for 15 minutes and weigh again. If constant weight is obtained, the apparatus is ready for use.

7.4.2 Weigh 2·0 g of the sample mixed with 2·0 g of a low carbon standard steel of known carbon content and place in a previously ignited combustion boat made of either porcelain, refractory, clay, nickel sheet or alumina and of dimensions about 100 × 20 × 15 mm with walls as thin as possible and cover the sample with lead foil

(1·5 g twice folded). Before placing the sample in the boat sprinkle in the bottom of the boat some burnt magnesite brick dust which has been tested by the blank run (*see* **7.4.3**). Insert the boat quickly into the hot zone of the furnace, with the rubber stopper replaced at the end of the combustion tube, wait for about a minute so that the boat attains the temperature of the furnace and pass a rapid stream (300 to 500 ml per minute) of oxygen for 10 to 15 minutes to sweep out carbon dioxide. At the end of this period, remove the carbon dioxide absorption bulb, cool in a desiccator and weigh quickly against a similar tube used as a counterpoise. The increase in weight represents carbon dioxide.

7.4.3 Carry out a blank determination on 2·0 g of the same low carbon standard steel that was mixed with the sample.

7.5 Calculation

$$\text{Carbon, percent} = \frac{(A - B) \times 27{\cdot}29}{C}$$

where

A = weight in g of carbon dioxide absorption tube after test,

B = weight in g of carbon dioxide absorption tube in blank run, and

C = weight in g of the sample taken.

8. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

8.1 Outline of the Method — The sample is burnt in a stream of pure oxygen, and the resulting carbon dioxide and excess oxygen after removal of the contaminants, are collected in a specially jacketed burette and the carbon dioxide absorbed in alkali. On passing the excess oxygen back to the burette, the dimunition in volume is read against a scale calibrated directly in percentages of carbon.

8.2 Apparatus — Assembly of the apparatus is shown in Fig. 2.

8.2.1 *Source of Oxygen Supply* — same as under **7.2.1**.

8.2.2 *Oxygen Purification Train* — consists of Arnold bottles (*B*) and (*C*) containing potassium hydroxide solution (30 percent) and concentrated sulphuric acid, respectively.

8.2.3 *Furnace* — a horizontal tube furnace (*D*) heated to 1 350°C.

8.2.4 *Combustion Tube* — same as under **7.2.4**.

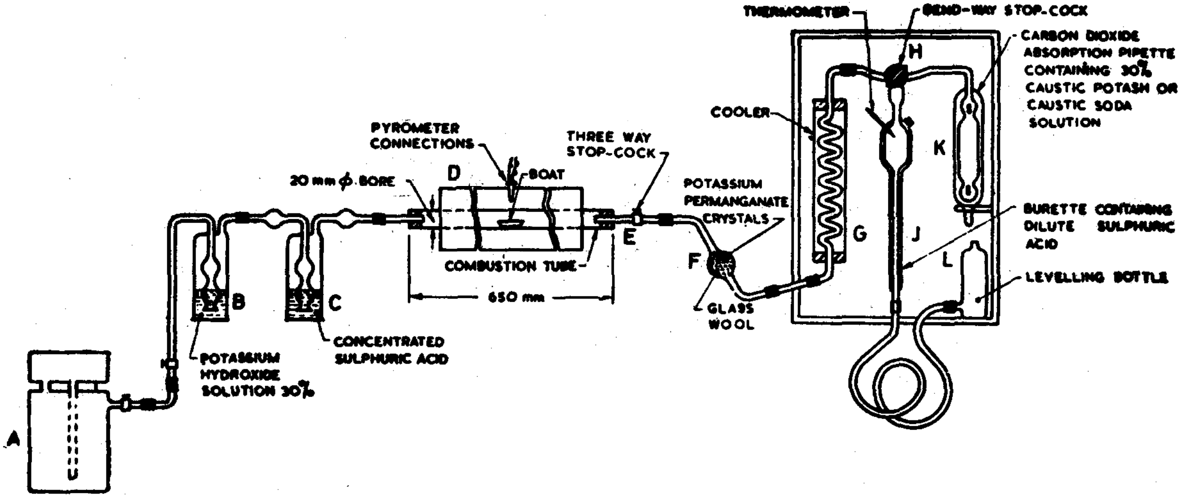

THERMOMETER
BEND-WAY STOP-COCK
H
CARBON DIOXIDE ABSORPTION PIPETTE CONTAINING 30% CAUSTIC POTASH OR CAUSTIC SODA SOLUTION
COOLER
K
PYROMETER CONNECTIONS
THREE WAY STOP-COCK
D
BOAT
20 mm ϕ BORE
POTASSIUM PERMANGANATE CRYSTALS
G
J
BURETTE CONTAINING DILUTE SULPHURIC ACID
E
F
L
COMBUSTION TUBE
LEVELLING BOTTLE
B
C
650 mm
GLASS WOOL
CONCENTRATED SULPHURIC ACID
POTASSIUM HYDROXIDE SOLUTION 30%
A

FIG. 2 APPARATUS FOR THE DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

8.2.5 *Absorption Train* — It consists of one 3-way stop-cock (*E*), a bulbed tubing (*F*) filled with potassium permanganate crystals and the exit end of which is packed with glass wool, one water-jacketed spiral cooling tube (*G*) and one bend-way manifold stop-cock (*H*) having one of its ends connected to the exit end of the combustion tube (*D*) through the spiral cooling tube (*G*), the bulbed tubing (*F*) and stop-cock (*E*). The other two ends of the stop-cock (*H*) are connected to the measuring burette (*J*) and an absorption pipette (*K*) in order to establish connection between (*J*) and (*G*) or between (*J*) and (*K*) as and when required. Before starting the combustion, by manipulating the stop-cocks (*H*) and (*E*) and the levelling bottle (*L*) connected with the burette the measuring burette (*J*) and the absorption pipette (*K*) should be filled, respectively with dilute sulphuric acid (2 : 98 by volume; coloured with a few drops of methyl orange) and sodium hydroxide or potassium hydroxide solution.

8.3 Reagents

8.3.1 *Sodium or Potassium Hydroxide Solution* — 30 percent (*w/v*).

8.3.2 *Concentrated Sulphuric Acid — see* **7.3.1**.

8.3.3 *Postassium Permanganate* — crystals.

8.3.4 *Magnesite Brick Powder — see* **7.3.11**.

8.3.5 *Dilute Sulphuric Acid* — 2 : 98 (*v/v*).

8.4 Procedure — Weigh accurately one gram of the sample in the form of small drillings, in a nickel, clay or porcelain boat 75 × 15 × 15 mm and introduce it into the heated combustion tube of the furnace (*D*) kept at 1 350°C. The boat shall be thinly lined with burnt magnesite brick powder. Close the furnace inlet with a rubber stopper, and let the boat attain the temperature of the furnace. Pass a stream of oxygen slowly into the furnace and establish connection with the burette which has been previously filled with acidulated water so that the liquid level in the bulbed portion of the gas burette does not fall rapidly. After a minute or so, the level of water in the burette begins to fall more rapidly though the same rate of flow of oxygen is maintained indicating completion of the combustion. Slow down the rate of flow of oxygen. Take reading when the level reaches near the zero graduation mark after closing the bend-way stop-cock and equalizing the levels of the burette and the connected levelling bottle. Pass the collected and measured gas several times into the absorbing pipette and, when absorption of carbon dioxide is complete, measure the contraction in the volume which, after proper temperature and pressure corrections, represents the percentage of carbon, when one gram of drillings is taken for analysis. On the basis of one gram of the sample taken for analysis, the burette is graduated to measure directly in percentage up to 1·5 percent carbon.

8.4.1 A standard steel of known carbon content shall be used for testing the apparatus.

9. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

9.1 Outline of the Method — After the removal of silica and reduction of ferric iron to ferrous state by zinc, sulphur is precipitated as barium sulphate by means of barium chloride in the acid medium.

9.2 Reagents

9.2.1 *Concentrated Nitric Acid* — *see* **6.3.1**.

9.2.2 *Hydrofluoric Acid* — 40 percent.

9.2.3 *Potassium Nitrate* — crystals.

9.2.4 *Boric Acid* — saturated solution.

9.2.5 *Concentrated Hydrochloric Acid* — *see* **5.3.3**.

9.2.6 *Zinc* (*20 to 30 mesh powder*) — sulphur-free.

9.2.7 *Dilute Hydrochloric Acid* — 1 : 99 (*v/v*).

9.2.8 *Barium Chloride Solution* — 10 percent (*w/v*).

9.2.9 *Hydrochloric Acid Wash Solution* — Dilute 5 ml of concentrated hydrochloric acid with water to 1 000 ml and add one gram of barium chloride.

9.3 Procedure

9.3.1 Transfer 5 g of the accurately weighed sample ground to pass through IS Sieve 15, to a 300-ml platinum dish provided with a cover. Add 50 to 60 ml of concentrated nitric acid and then one to two millilitres of hydrofluoric acid. Warm, if necessary, to start the reaction. Stop heating when it gets attacked and add small portions of hydrofluoric acid from time to time until decomposition is complete (usually 50 to 60 ml of hydrofluoric acid are required). Add 2 g of potassium nitrate and evaporate to a small volume (3 to 5 ml). Add 10 to 15 ml of concentrated nitric acid and evaporate once again to a small volume to ensure the complete removal of hydrofluoric acid. Now add 25 ml of boric acid solution and digest for 15 minutes at about 90°C. Transfer the solution to a porcelain vessel, evaporate to dryness and bake at 120°C. Dissolve the residue in 50 ml of concentrated hydrochloric acid and again evaporate to dryness. Treat with 30 ml of concentrated hydrochloric acid.

9.3.2 Evaporate to a syrupy consistency and add 5 ml of concentrated hydrochloric acid, 50 ml of hot water and 5 g of zinc. Warm on steam-bath until iron is reduced to the ferrous state and evolution of hydrogen ceases. Filter through a close texture filter paper and wash 3 to 4 times with hot dilute hydrochloric acid.

9.3.3 Concentrate the filtrate to adjust the acidity to 2 percent by volume of hydrochloric acid. Warm it to 60 to 70°C and add 10 ml of barium chloride solution dropwise with constant stirring. Let the solution stand for two hours at steam-bath and overnight at the room temperature. Filter through filter paper No. 42, washing the precipitate from the beaker with a jet of cold hydrochloric acid wash solution. Wash until the filtrate is free from iron salts, and continue washing with cold water until chlorides are removed. Transfer the pad and precipitate to a platinum or porcelain crucible.

9.3.4 Dry the filter pad completely at a low temperature (in the mouth of a muffle furnace) until the paper chars and gently burns; ignite finally at a temperature of 800 to 900°C to constant weight.

9.3.5 Carry out a blank determination following the same procedure and using the same quantity of all reagents but without the sample.

9.4 Calculation

$$\text{Sulphur, percent} = \frac{(A - B) \times 13{\cdot}74}{C}$$

where

A = weight in g of the barium sulphate obtained in **9.3.4**,

B = weight in g of barium sulphate obtained in the blank determination, and

C = weight in g of the sample taken.

10. DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

10.1 Outline of the Method — From the acid solution of the sample, ammonium phospho-molybdate is precipitated, filtered, dissolved in excess of sodium hydroxide solution and the unreacted alkali back-titrated with standard hydrochloric acid.

10.2 Reagents

10.2.1 *Concentrated Nitric Acid — see* **6.3.1.**

10.2.2 *Hydrofluoric Acid* — 40 percent.

10.2.3 *Dilute Sulphuric Acid* — 1 : 1 (*v/v*).

10.2.4 *Concentrated Hydrochloric Acid* — *see* **5.3.3**.

10.2.5 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

10.2.6 *Dilute Nitric Acid* — 1 : 1, 1 : 99 and 2 : 98 (*v/v*).

10.2.7 *Sulphurous Acid* — Saturate water with sulphur dioxide. Prepare fresh as needed.

10.2.8 *Potassium Permanganate Solution* — 2·5 percent (*w/v*).

10.2.9 *Potassium Nitrite* — solid.

10.2.10 *Ammonium Molybdate Solution* — Add solution (*A*) (*see* **10.2.10.1**) slowly and with constant stirring to solution (*B*) (*see* **10.2.10.2**) kept cool in a cold water-bath. Add 10 ml of ammonium phosphate (one gram per litre) and keep the solution at least for 24 hours. Filter the solution through filter paper No. 1 before use.

10.2.10.1 *Solution* (*A*) — Dissolve 100 g of molybdic acid (MoO_3, 85 percent) or 118 g of ammonium molybdate in a mixture of 145 ml of concentrated ammonium hydroxide and 270 ml of water. Cool the solution.

10.2.10.2 *Solution* (*B*) — Add 490 ml of concentrated nitric acid to 1 150 ml of water and cool.

10.2.11 *Concentrated Sulphuric Acid* — *see* **3.1**.

10.2.12 *Perchloric Acid* — 70 percent.

10.2.13 *Dilute Hydrochloric Acid* — 1 : 1 (*v/v*).

10.2.14 *Hydrobromic Acid* — 48 percent.

10.2.15 *Potassium Nitrate Wash Solution* — one percent (*w/v*).

10.2.16 *Sodium Hydroxide Solution* — 0·1 N. Dissolve 4·5 g of purified sodium hydroxide in one litre of freshly boiled and cooled distilled water, add a slight excess of barium hydroxide solution, let stand for twenty four hours and decant the liquid before use.

10.2.17 *Phenolphthalein Indicator Solution* — 0·2 percent (*w/v*) in rectified spirit.

10.2.18 *Standard Hydrochloric Acid Solution* — 0·1 N. Dilute 11 ml of concentrated hydrochloric acid to one litre and standardize the solution against sodium carbonate.

10.3 Procedure

10.3.1 Transfer 2 g of an accurately weighed sample to a 300-ml platinum dish provided with a cover and add 25 ml of concentrated nitric acid. Add 2 ml of hydrofluoric acid, warm until violent reaction begins, stop heating and add hydrofluoric acid from time to time until decomposition is complete. Add 10 ml of dilute sulphuric acid and evaporate to fum . Cool slightly and carefully. Add 100 ml of warm water and 10 ml of concentrated hydrochloric acid. Warm to dissolve salts, transfer the solution to a 600-ml beaker and dilute to 300 ml. Add concentrated ammonium hydroxide in slight excess, heat to boiling, filter and wash the precipitate moderately with hot water. Transfer as much of the precipitate as possible to a 300-ml Erlenmeyer flask and dissolve in 75 ml of hot dilute hydrochloric acid which is poured through the paper and funnel. Wash with hot water and collect the washings in the beaker keeping the bulk as low as possible.

10.3.2 Add 5 g of ammonium bromide and with the cover of beaker removed evaporate the solution until white fumes appear and volume is reduced to 4 ml. Add 10 ml of concentrated nitric acid and warm gently until all bromine is expelled. Dilute with 40 ml of water, heat to boiling and oxidize with potassium permanganate solution. Redissolve the precipitated manganese with few drops of potassium nitrite solution, boil thoroughly and cool.

10.3.3 Add concentrated ammonium hydroxide in slight excess. Just redissolve the precipitate by the cautious addition of 4 to 5 ml of concentrated nitric acid and add 4 ml in excess. Adjust the temperature of the solution to 70 to 80°C, add 40 ml of filtered ammonium molybdate solution, shake the solution until the precipitate forms and allow to stand for one hour.

10.3.4 Filter the yellow ammonium phosphomolybdate precipitate through filter paper pulp and wash with cold dilute nitric acid solution (2 : 98).

10.3.5 Wash three to four times with cold dilute nitric acid (1 : 99). Wash with potassium nitrate wash solution until 10 ml of the filtrate collected in a test tube do not consume more than one drop of the alkali solution, using phenolphthalein indicator solution, showing the filtrate to be free of acid. When the washing is complete, transfer the filter paper pulp alongwith the precipitate to the original beaker in which the precipitation was done. Add with stirring a measured excess of sodium hydroxide solution until all the yellow precipitate has dissolved and the solution is colourless. Add 50 to 60 ml of water and about five millilitres of sodium hydroxide solution in excess and stir. Add three to four drops of phenolphthalein indicator solution and titrate with the standard hydrochloric acid solution, until the pink colour is completely discharged.

10.3.6 Carry out a blank on the same quantity of sodium hydroxide solution which was added in the test, by titrating it with the standard hydrochloric acid solution, using three to four drops of phenolphthalein indicator solution.

10.4 Calculation

$$\text{Phosphorus, percent} = \frac{(A - B)\ C \times 0{\cdot}135}{D}$$

where

A = volume in ml of the standard hydrochloric acid solution required for the blank test,

B = volume in ml of the standard hydrochloric acid solution required to titrate the excess,

C = normality of the standard hydrochloric acid solution, and

D = weight in g of the sample taken.

11. DETERMINATION OF ALUMINIUM BY THE THIOSULPHATE PHOSPHATE METHOD

11.1 Outline of the Method — After the removal of silica, aluminium is precipitated by ammonium phosphate in presence of sodium thiosulphate which reduces ferric iron to ferrous state. The precipitate is ignited, fused with sodium carbonate and extracted. Aluminium is re-precipitated from the extract as aluminium phosphate, filtered and ignited to constant weight.

11.2 Reagents

11.2.1 *Hydrofluoric Acid* — 40 percent.

11.2.2 *Concentrated Nitric Acid* — *see* **6.3.1**.

11.2.3 *Dilute Sulphuric Acid* — 1 : 1 (*v/v*).

11.2.4 *Concentrated Hydrochloric Acid* — *see* **5.3.3**.

11.2.5 *Ammonium Acetate Solution* — 10 percent (*w/v*).

11.2.6 *Ammonium Phosphate Solution* — 10 percent (*w/v*).

11.2.7 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

11.2.8 *Sodium Thiosulphate* — crystals.

11.2.9 *Ammonium Nitrate Solution* — 5 percent (*w/v*).

11.2.10 *Sodium Carbonate* — anhydrous.

11.2.11 *Potassium Nitrate* — solid.

11.2.12 *Sodium Hydroxide Solution* — one percent (*w/v*).

11.2.13 *Sodium Sulphate Solution* — 2 percent (*w/v*).

11.3 Procedure

11.3.1 Transfer 5 g of the accurately weighed sample ground to pass through IS Sieve 15, to a 300-ml platinum dish provided with a cover, and moisten with water. Add 2 to 3 ml of hydrofluoric acid at a time until about 75 ml have been added. Then add 15 ml of concentrated nitric acid to complete the decomposition. When reaction is complete rinse and remove the cover. Add 25 ml of dilute sulphuric acid and evaporate until fumes of sulphur trioxide come off freely. Cool slightly, cautiously rinse down the sides of the dish and again heat to fumes. Cool and carefully add 100 ml of water and 10 ml of concentrated hydrochloric acid. Warm until salts have been dissolved and transfer the solution to a 600-ml beaker.

11.3.2 Dilute to about 400 ml, add 10 ml of ammonium acetate solution and 20 ml of ammonium phosphate solution. Neutralize the solution by adding concentrated ammonium hydroxide until a slight permanent precipitate is obtained. Clear the solution with a minimum of concentrated hydrochloric acid and add 2 ml in excess. Boil the solution and add 10 g of sodium thiosulphate. Boil for 30 minutes, filter and wash with ammonium nitrate solution. Redissolve the precipitate on the filter paper in hot concentrated hydrochloric acid and wash the residue 7 to 8 times with hot water. Re-precipitate aluminium from the solution, filter and wash the precipitate with ammonium nitrate solution.

11.3.3 Ignite the residue in a platinum crucible, fuse with a mixture of 4 g of sodium carbonate and one gram of potassium nitrate, leach the melt with water containing a few drops of sodium hydroxide solution, and filter. Wash the paper and residue with sodium sulphate solution. Ignite the residue and fuse and extract with water a second time and combine the two filtrates. Discard the residue.

11.3.4 Add dilute sulphuric acid to slight excess and bring to the boil. Add 5 ml of ammonium phosphate solution and render it slightly ammoniacal. Maintain at 60°C for at least 30 minutes, filter through pulp, wash with hot ammonium nitrate solution and finally with hot water. Ignite the paper and residue strongly in a weighed porcelain crucible. If the residue is discoloured, evaporate with 2 ml of concentrated nitric acid to dryness and re-ignite the aluminium phosphate to constant weight.

11.4 Calculation

$$\text{Aluminium, percent} = \frac{A \times 22{\cdot}11}{B}$$

where

A = weight in g of aluminium phosphate obtained, and
B = weight in g of the sample taken.

SECTION II FERROCHROMIUM

12. DETERMINATION OF CHROMIUM BY THE PEROXIDE FUSION (VOLUMETRIC) METHOD

12.1 Outline of the Method — The sample is decomposed by sodium peroxide fusion and chromium in the solution of the sample is reduced by measured amount of ferrous ammonium sulphate solution. The excess of the latter is titrated with either standard dichromate solution or standard permanganate solution.

12.2 Apparatus — nickel crucible (30-ml capacity) and nickel rods.

12.3 Reagents

12.3.1 *Sodium Peroxide* — solid.

12.3.2 *Dilute Sulphuric Acid* — 1 : 4 (*v/v*).

12.3.3 *Potassium Permanganate Solution* — 2 percent (*w/v*).

12.3.4 *Manganese Sulphate Solution* — 10 percent (*w/v*).

12.3.5 *Standard Ferrous Ammonium Sulphate Solution* — 0·2 N. Dissolve 78·4 g of pure ferrous ammonium sulphate crystals [$FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$] in cold sulphuric acid (1 : 19) and make up to one litre with this acid. Standardize against standard potassium dichromate (0·2 N) or standard potassium permanganate (0·2 N) as described under **12.3.9**. Prepare fresh as needed.

12.3.6 *Phosphoric Acid* — 85 percent.

12.3.7 *Standard Potassium Dichromate Solution*—0·2 N. Dissolve 9·808 g of Analar grade potassium dichromate in water and make up the solution to one litre in a volumetric flask. Mix thoroughly by pouring back and forth at least four times into a beaker which is clean and dry at the start.

12.3.8 *Sodium Diphenylamine Sulphonate Indicator Solution* — Dissolve 0·32 g of barium diphenylamine sulphonate in 100 ml of hot water. Add 0·5 g of sodium sulphate, stir and filter off the precipitate of barium sulphate. Store in a dark-coloured bottle.

12.3.9 *Standard Potassium Permanganate Solution* — 0·2 N. Dissolve 6·4 g of potassium permanganate in one litre of water. Let stand in the dark for 2 weeks and filter without washing through a Gooch crucible or fritted glass crucible of fine porosity avoiding contact with rubber or other organic material. Store in a dark coloured, glass-stoppered bottle. Standardize against Analar grade sodium oxalate by weighing 0·268 g of the salt, dissolving it in 250 ml of dilute sulphuric acid (5 : 95) and titrating against the permanganate solution at 55 to 60°C to a faint pink end-point. Adjust the strength of the permanganate solution such that 0·268 g of sodium oxalate requires exactly 20 ml of the permanganate solution.

12.4 Procedure

12.4.1 Mix intimately 0·5 g of the sample (ground to pass IS Sieve 15) with 8 g of sodium peroxide in a nickel crucible with nickel rod and clean the rod with another rod. Cover the mixture with 2 g of sodium peroxide and then cover with a nickel cover. Carefully fuse at a dull red heat for 5 minutes till the mass has melted and rotate the crucible in order to stir up any unattacked particles. Allow the crucible to cool.

12.4.2 Transfer to a 600-ml covered beaker containing about 250 ml of water, and after extraction of the melt, remove the crucible and the cover and rinse thoroughly. Boil the contents of the beaker briskly for 10 minutes, cool, treat with dilute sulphuric acid to 50 ml excess and raise to boiling. If there is no pink colouration or brown precipitate of manganese dioxide treat with sufficient potassium permanganate solution to cause a definite pink colouration. Boil for 5 minutes and add 5 ml of manganese sulphate solution and boil for a further 5 minutes. Cool somewhat and filter through a close texture filter paper into a 1-litre Erlenmeyer flask. Wash the filter with hot water.

12.4.3 Cool and run-in a measured excess of standard ferrous ammonium sulphate solution (1·25 ml of 0·2 N solution is roughly equivalent to one percent chromium on a 0·5 g sample). The point at which reduction is complete can be detected by the change in the deep green colour that is developed. Add 5 ml of phosphoric acid and titrate the excess ferrous ammonium sulphate with standard potassium dichromate solution using sodium diphenylamine sulphonate as indicator.

12.4.4 Alternatively, the excess can also be titrated with standard potassium permanganate solution taking the first faint permanent darkening of the clear green colour as the end point. Preserve the titrated solution for running the blank.

12.4.5 Determine the blank by running in the same volume of ferrous ammonium sulphate solution as was used in the above estimation into the flask containing the titrated solution reserved under **12.4.4** and titrate with standard potassium dichromate or potassium parmanganate to the same end point.

12.5 Calculation

$$\text{Chromium, percent} = \frac{(A-B)\,C \times 1{\cdot}734}{D}$$

where

A = volume in ml of the standard potassium dichromate or permanganate solution required for the blank,

B = volume in ml of the standard potassium dichromate or permanganate solution required for the excess ferrous ammonium sulphate,

C = normality of the standard potassium dichromate or permanganate solution used, and

D = weight in g of the sample taken.

13. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION (GRAVIMETRIC) METHOD

13.1 Determine the carbon content of the sample by following the method as described under 7, with the following modifications.

13.1.1 Use 0·25 to 0·5 g of the sample (1·5 to 2 g in case of low-carbon ferrochromium).

13.1.2 Use a furnace temperature between 1 250 to 1 300°C.

13.1.3 Place a copper roll in the form of gauze at the end of combustion tube to reduce oxides of nitrogen.

14. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

14.1 Outline of the Method — The sample is fused with sodium peroxide and the fused mass evaporated with hydrochloric acid, baked and then estimated by hydrofluorization as usual.

14.2 Apparatus — nickel crucible 50-ml capacity and nickel rods.

14.3 Reagents — In addition to the reagents given under **5.3**, the following reagents are required.

14.3.1 *Sodium Carbonate* — anhydrous.

14.3.2 *Sodium Peroxide* — solid.

14.4 Procedure

14.4.1 Line a 50-ml nickel crucible with sodium carbonate by fusing one gram of the substance at about 1 100°C and running the melt up the sides as it cools. Add 3 g of sodium peroxide, heat until the mass is molten; let it solidify on the bottom of the crucible. Transfer 2 g of the accurately weighed sample and 15 g of sodium peroxide to the crucible, mix thoroughly with a nickel rod, taking care to clean the rod with another rod. Cover and fuse at a dull red heat in an electrically heated muffle furnace. Allow it to cool till the fused mass has solidified; loosen the cake by tapping while still warm. Extract the fused mass with minimum quantity of hot water, cool and acidify with concentrated hydrochloric acid. Transfer the extract to a dry 250-ml porcelain casserole. Cover and immediately add 80 ml of dilute hydrochloric acid (1 : 1).

14.4.2 Carry out baking as under **5.4.2** and **5.4.3.** Further complete the estimation as described under **5.4.4** to **5.5.**

15. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

15.1 Outline of the Method — After the removal of silica, chromium in the filtrate is reduced and sulphur precipitated by the addition of barium chloride. The precipitate is ignited, fused with sodium carbonate and the fused mass extracted with water. Sulphur in the acid solution is then precipitated as barium sulphate and estimated as usual.

15.2 Apparatus — nickel crucible, 50-ml capacity with nickel rods.

15.3 Reagents — In addition to the reagents given under **9.2** and **14.3,** the following reagents are required.

15.3.1 *Hydrogen Peroxide* — 20 volumes.

15.3.2 *Dilute Hydrochloric Acid* — 1 : 20 (*v/v*).

15.4 Procedure

15.4.1 Fuse 5 g of the accurately weighed sample with 40 g of sodium peroxide in a nickel crucible lined with sodium carbonate as under **14.4.1.** Extract the fused mass with minimum quantity of hot water. Cool and acidify with concentrated hydrochloric acid. Evaporate the solution to dryness. Carry out baking at 100 to 110°C for half an hour. Allow to cool a little and extract the mass with 20 ml of concentrated hydrochloric acid by warming gently, and dilute with 150 ml of water. Boil gently to dissolve all salts and filter through filter paper No. 40. Wash the paper and residue several times with hot dilute hydrochloric acid and finally with warm water. Preserve the filtrate.

15.4.2 To the filtrate from **15.4.1**, add 10 ml of barium chloride solution dropwise with constant stirring. Let the solution stand for two hours at steam-bath and overnight at the room temperature. Filter through a close texture paper, wash the precipitate with warm water and ignite in a platinum crucible.

15.4.3 Add 2 g of sodium carbonate in the platinum crucible, cover and then fuse the ignited residue under sulphur-free conditions in electrically heated muffle furnace. Cool, dissolve the melt in 50 to 60 ml of hot water, filter and wash with warm water. Add 10 to 15 ml of hydrogen peroxide and further proceed as described under **9.3.2** to **9.4** to estimate sulphur.

16. DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

16.1 Outline of the Method — The sample is decomposed with sodium peroxide and phosphorus is precipitated from the acid solution of the sample as phosphomolybdate and estimated as usual.

16.2 Apparatus — nickel crucible of 50-ml capacity.

16.3 Reagents — In addition to the reagents given under **10.2**, the following reagents are required.

16.3.1 *Sodium Carbonate* — anhydrous.

16.3.2 *Sodium Peroxide* — solid.

16.3.3 *Dilute Hydrochloric Acid* — 5 : 95 (*v/v*).

16.4 Procedure

16.4.1 Fuse 2 g of an accurately weighed sample with 15 g of sodium peroxide in a 50-ml nickel crucible (lined with sodium carbonate) and extract the fused mass as described under **14.4.1**.

16.4.2 Rinse the crucible with hot dilute hydrochloric acid (5 : 95) and add to the casserole. When the reaction is complete, rinse and remove the cover. Complete the estimation as described under **10.3.3** to **10.4**.

17. DETERMINATION OF NITROGEN BY THE STEAM DISTILLATION METHOD

17.1 Outline of the Method — The sample is decomposed with sulphuric acid and the nitrogen fixed as ammonium sulphate. It is then boiled with sodium hydroxide and ammonia distilled. It is absorbed in boric acid and the distillate titrated with standard sulphuric acid.

17.2 Apparatus

17.2.1 Decomposition of the sample should be carried out in a 250-ml flask fitted with a ground neck carrying a 45 cm long air condenser.

17.2.2 The steam distillation shall be carried out in an assembly shown in Fig. 3.

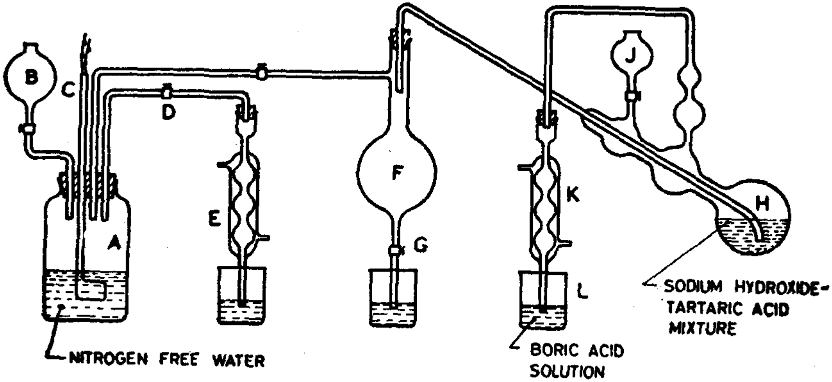


FIG. 3 APPARATUS FOR DETERMINATION OF NITROGEN BY THE STEAM DISTILLATION METHOD

17.3 Reagents

17.3.1 *Nessler's Reagent* — To 95 ml of potassium iodide solution (25 percent), add with shaking a saturated solution of mercuric chloride until a permanent precipitate is obtained. Make small additions of potassium iodide solution until the precipitate is almost redissolved, followed by a solution of 60 g of potassium hydroxide in 60 ml of water. Add cautiously mercuric chloride solution until a slight permanent yellow precipitate is formed. Dilute to 400 ml and allow to stand overnight before filtering into a stock bottle.

17.3.2 *Nitrogen-Free Water* — Add a few pellets of caustic potash and 0·5 g of Devarda's alloy (*see* **17.3.10**) per litre of distilled water, heat on the hot-plate for four hours and finally distil in an all-glass unit rejecting the first 100-ml portion of the distillate. Confirm the absence of ammonia in the distillate by testing a few millilitres with Nessler's reagent before collecting it for use.

17.3.3 *Potassium Sulphate* — crystals.

17.3.4 *Copper Sulphate* — crystals.

17.3.5 *Dilute Sulphuric Acid* — 1 : 4 (*v/v*). To 800 ml of nitrogen-free water, add cautiously 200 ml of concentrated sulphuric acid previously tested for freedom from nitrates by the brucine test.

17.3.6 *Barium Chloride Solution* — 2 percent.

17.3.7 *Concentrated Sulphuric Acid — see* **7.3.1.**

17.3.8 *Mixed Indicator Solution* — Dissolve 0·075 g of bromocresol green and 0·05 g of methyl red in 100 ml of methanol.

17.3.9 *Selenium Metal* — pure.

17.3.10 *Devardd s Alloy* — 50 Cu, 5 Al, 5 Zn.

17.3.11 *Boric Acid Solution* — 0·1 percent in nitrogen-free water.

17.3.12 *Sodium Hydroxide-Tartaric Acid Solution* — To one litre of nitrogen-free water, add 500 g of sodium hydroxide and 133 g of tartaric acid. Warm gently to complete solution. Add one gram of Devarda's alloy, boil for 45 minutes, cool and dilute to 1 250 ml with nitrogen-free water.

17.3.13 *Sodium Hydroxide Solution* — 0·01 N. Dissolve 0·5 g of sodium hydroxide pellets in one litre of freshly boiled and cooled distilled water. Dissolve 0·400 0 g of potassium acid phthalate in one litre of freshly boiled and cooled distilled water. Standardize the sodium hydroxide solution against the potassium acid phthalate solution, using phenolphthalein indicator, and render it equivalent to the phthalate solution.

17.3.14 *Standard Sulphuric Acid* (1 ml = 0·000 07 g of N_2) — 0·005 N. Add three millilitres of dilute sulphuric acid (1 : 9) to 500 ml of water and dilute to one litre, standardize the dilute sulphuric acid against standard sodium hydroxide solution (0·01 N), using phenolphthalein as indicator. Render it equivalent to the standard alkali solution by dilution with water. Dilute 50 ml of this acid to 100 ml in a volumetric flask.

17.4 Procedure

17.4.1 Wash the sample with nitrogen-free water, alcohol and finally with ether. Dry it thoroughly and transfer one gram of the sample to a 250-ml round-bottom flask. Add 5 g of potassium sulphate crystals and one small crystal of copper sulphate and 50 ml of dilute sulphuric acid. Attach an air condenser and digest gently over a broad flame until the decomposition is complete. Evaporate to fumes, cool, dilute with 35 ml of water, warm to redissolve separated salts. If a dark-coloured insoluble residue remains, allow to settle after the addition of 5 ml of barium chloride solution. Decant off the clear solution into a beaker and treat the residue in the flask with 5 ml of concentrated sulphuric acid and 2 g of potassium sulphate. Heat strongly, and fume until all the dark-coloured particles are decomposed. The process can generally be hastened by the addition of 0·1 g of selenium metal before fuming. Dilute and mix with first portion of the solution. Preserve the solution.

17.4.2 Charge the steam generator (*A*) with nitrogen-free water through the dropping funnel (*B*), switch on the immersion heater (*C*) and allow steam to issue freely from the flask (*F*) by keeping the stop-cock (*G*) open. Add 20 ml of sodium hydroxide-tartaric acid mixture to the flask (*H*) through the funnel (*J*), close the stop-cock (*G*), allow steam to bubble through the mixture for five minutes. Regulate the flow of steam through the mixture by means of stop-cock (*D*) which provides for the escape of the excess of steam. This can be condensed by the condenser (*E*) and returned to the steam generator at regular intervals. At the end of the steaming period, switch off the heater and allow the contents of the flask (*H*) to syphon into the flask (*F*) and drain out through the tap (*G*).

17.4.3 Place 10 ml of boric acid solution in beaker (*L*) and raise it until the lower end of the condenser (*K*) dips into the solution. Pour the solution of the sample, reserved in accordance with **17.4.1**, into the distillation flask (*H*) through the funnel (*J*). Rinse the beaker with a little ammonia-free water, in the flask (*H*), and then add 100 ml of sodium hydroxide-tartaric acid mixture. Stopper the top of the funnel (*J*), switch on the heater (*C*) and close the tap (*G*), as soon as the steam starts escaping through it. Adjust a proper flow of cooling water through the condenser (*K*) and distil as rapidly as possible, collecting 60 to 70 ml of the distillate, indicated by mark on the receiver.

17.4.4 Add three drops of the mixed indicator to the distillate and titrate against standard sulphuric acid (0·005 N). Note the volume of the acid consumed by the solution, when it changes from green to wine-red.

17.4.5 Make a blank determination following the same procedure and using the same amounts of all reagents. The blank should not exceed the equivalent of 0·5 ml of standard sulphuric acid (0·005 N). If higher blanks are recorded, their origin should be traced and eliminated.

17.5 Calculation

$$\text{Nitrogen, percent} = \frac{(A - B) \times 0{\cdot}007}{C}$$

where

A = volume in ml of the standard sulphuric acid (0·005 N) consumed by the sample,

B = volume in ml of the standard sulphuric acid (0·005 N) consumed by the blank run, and

C = weight in g of the sample taken.

SECTION III FERROMANGANESE AND SPEIGELEISEN

18. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

18.1 Outline of the Method — The sample is decomposed with nitric acid and baked with hydrochloric acid and filtered. Silica is then determined by hydrofluorization as usual.

18.2 Reagents — In addition to the reagents given under **5.3**, the following reagent is required.

18.2.1 *Dilute Nitric Acid* — 1 : 3 (*v/v*).

18.3 Procedure

18.3.1 Weigh exactly one gram of the sample into a 500-ml conical beaker. Add to it about 30 ml of concentrated nitric acid, simultaneously covering the container by a watch-glass. Set the contents for decomposition and dissolution on a hot-plate till all the sample has gone into solution (as is seen from the absence of particles of ferromanganese in the beaker and clear solution of the sample in the beaker). Dry and bake as under **5.4.2** and **5.4.3**. Reserve the filtrate that will be obtained by following **5.4.3** for the estimation of manganese. Complete the estimation as described under **5.4.4** to **5.5**.

19. DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD

19.1 Outline of the Method — Bivalent manganese in the filtrate from silicon determination is oxidized to permanganic acid by the use of sodium bismuthate. Manganese is then estimated by the use of ferrous sulphate and potassium permanganate solutions.

19.2 Reagents

19.2.1 *Dilute Nitric Acid* — 3 : 97 (*v/v*).

19.2.2 *Concentrated Sulphuric Acid* — *see* **7.3.1**.

19.2.3 *Sulphurous Acid Solution* — Make 5 percent (approximately) solution of sulphur dioxide in water. Prepare fresh as needed.

19.2.4 *Sodium Bismuthate* — 80 percent solution and solid.

19.2.5 *Ferrous Ammonium Sulphate Solution* — 0·1 N approximately. Dissolve 39·2 g of ferrous ammonium sulphate crystals [$FeSO_4$. $(NH_4)_2SO_4$, $6H_2O$] in cold dilute sulphuric acid (5 : 95) and make up to one litre with this acid. Mix well and keep in an amber-coloured glass-stoppered bottle.

19.2.6 *Phosphoric Acid* — 85 percent.

19.2.7 *Standard Potassium Permanganate Solution* — 0·1 N. Dissolve 3·2 g of potassium permanganate in one litre of water. Let stand in the dark for two weeks and filter without washing through a Gooch crucible or fritted glass crucible of fine porosity avoiding contact with rubber or other organic material. Store in a dark-coloured, glass-stoppered bottle. Standardize against Analar sodium oxalate by weighing 0·134 g of the salt, dissolving it in 250 ml of dilute sulphuric acid (5 : 95) and titrating against the permanganate at 55 to 60°C to a faint pink end point. Adjust the strength of the permanganate solution such that 0·134 g of sodium oxalate requires exactly 20 ml of permanganate solution.

For Volhard's titration it is preferable to standardize the permanganate against standard ferromanganese or manganese ore of known manganese content.

19.3 Procedure

19.3.1 Take the solution reserved under **18.3.1** and evaporate with 10 ml of concentrated sulphuric acid to fumes. Cool, dilute to 100 ml cautiously and boil until all the salts are in solution. Transfer to 500-ml flask and make up to the mark. Use suitable aliquots for determination of manganese by Bismuthate or Volhard method.

19.3.2 Pipette out exactly 25 ml of the solution (or such portion that will contain about 0·03 g of manganese) into a 500-ml beaker. Add about 50 ml of concentrated nitric acid, heat to boiling, remove from the heat and add sodium bismuthate a little at a time until a precipitate of manganese dioxide has formed. When this occurs, add sulphurous acid dropwise until the precipitate has dissolved. Boil the solution for about 5 minutes to completely expel oxides of nitrogen and cool to 10 to 15°C.

19.3.3 To the cold solution add about 1 to 2 g of sodium bismuthate and agitate briskly for one minute; filter immediately through a Gooch crucible. Wash with cold dilute nitric acid until the washings are colourless. Reject the insoluble residue. The temperature of the filtrate shall be maintained between 10 to 15°C. To the filtrate, add a measured excess of ferrous ammonium sulphate solution

(50 ml will suffice) and stir. Add 2 ml of syrupy phosphoric acid and immediately titrate with the standard potassium permanganate solution until a faint and permanent pink colour appears.

19.3.4 Carry out a blank determination through all stages using the same amount of ferrous ammonium sulphate and phosphoric acid and titrate with standard permanganate solution.

19.4 Calculation

$$\text{Manganese, percent} = \frac{(A-B)\,C\times 1{\cdot}10}{D}$$

where

A = volume in ml of the standard permanganate solution required to titrate the blank,

B = volume in ml of the standard permanganate solution required to titrate the excess ferrous ammonium sulphate,

C = normality of the standard permanganate solution, and

D = weight in g of the sample represented by the aliquot taken.

20. DETERMINATION OF MANGANESE BY THE VOLHARD (ALTERNATE) METHOD

20.1 Outline of the Method — Iron hydroxide in the filtrate from silicon determination is precipitated by means of zinc oxide and filtered. Bivalent manganese in the filtrate is determined by its oxidation to quadrivalent state with standard permanganate solution.

20.2 Reagents

20.2.1 *Concentrated Sulphuric Acid — see* **7.3.1.**

20.2.2 *Sodium Carbonate Solution* — Dissolve 318 g of anhydrous sodium carbonate in water and make up to one litre.

20.2.3 *Zinc Oxide Emulsion* — Make a suspension of finally divided zinc oxide by thoroughly shaking 50 g of the reagent in 300 ml of water. Prepare fresh as required.

20.2.4 *Concentrated Nitric Acid — see* **6.3.1.**

20.2.5 *Standard Potassium Permanganate Solution* — 0·1 N. *See* **19.2.7.**

20.3 Procedure

20.3.1 Pipette out 25 ml of the solution prepared under **19.3.1** (for lower percentages a suitable aliquot may be taken) into a 500-ml conical flask. Add in small amounts zinc oxide emulsion until a point is reached where the liquid suddenly coagulates. Dilute the contents to 200 ml; boil and add 2 to 3 drops of concentrated nitric acid and titrate against standard potassium permanganate solution.

20.3.2 The permanganate causes a precipitate which clouds the liquid, and it is therefore necessary to titrate cautiously and agitate the flask after each addition and then allow the precipitate to settle sufficiently to observe whether or not the solution is coloured pink. (When the supernatant liquid shows persistent pink tinge, bring the contents of the flask nearly to a boil once more and again observe if the pink tinge still persists, adding permanganate solution, if necessary.) In making this end test, avoid actually boiling the liquid, as a continual destruction of the colour may sometimes thus be affected and the end point considerably passed. When the colour remains permanent, the end point is reached. Thus three separate titrations shall be made, the first two titrations being done to obtain pilot reading so that in the final titration all the permanganate required can be added as rapidly as possible and the colour observed.

20.4 Calculation

$$\text{Manganese, percent} = \frac{AB \times 1{\cdot}666}{C}$$

where

A = volume in ml of the standard permanganate solution consumed,

B = normality of the standard permanganate solution, and

C = weight in g of the sample represented by the aliquot used.

21. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION (GRAVIMETRIC) METHOD

21.1 Determine the carbon content of the sample by following the method as described under **6**, with the following modifications.

21.1.1 Use 0·25 g of the sample.

21.1.2 Use furnace temperature of 1 150 to 1 200°C.

22. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

22.1 Outline of the Method — The sample is dissolved in nitric acid and evaporated to dryness with hydrochloric acid. Sulphur is then precipitated as barium sulphate.

22.2 Reagents — In addition to the reagents given under **9.2**, the following reagent is required.

22.2.1 *Potassium Nitrate* — crystals.

22.3 Procedure

22.3.1 Transfer 5 g of the accurately weighed sample into a 600-ml beaker. Add a few crystals of potassium nitrate and 50 to 60 ml of concentrated nitric acid. Carefully pour in 25 ml of concentrated hydrochloric acid and evaporate to dryness. Bake on a hot-plate for 30 minutes. Cool, add 30 ml of concentrated hydrochloric acid, warm gently until salts are dissolved and proceed further as described under **9.3.2** to **9.4** to estimate sulphur.

23. DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

23.1 Outline of the Method — After the removal of silica, phosphorus in the acid solution of the sample is precipitated as phosphomolybdate and then estimated as usual.

23.2 Reagents — same as under **10.2**.

23.3 Procedure

23.3.1 Weigh accurately the sample as described in the following table depending upon the percentage of phosphorus in the sample and transfer to a 400-ml beaker, cover it with 15 ml of concentrated nitric acid and add cautiously 10 ml of concentrated hydrochloric acid at such a rate that the liquid when frothing, does not overflow:

Phosphorus Content Percent	*Weight of Sample*
Below 0·35	1 g
0·35 to 0·60	0·50 g
1	0·25 g

Digest until dissolved, evaporate to dryness and bake for 20 minutes at a temperature of about 150°C. Cool, take up the mass in 20 ml of concentrated hydrochloric acid and boil until a clear solution is obtained. Dilute with 20 ml of water and filter into a 400-ml beaker, washing the paper and residue with small quantities of dilute hydrochloric acid. Preserve the filtrate.

23.3.2 Ignite the paper and residue in a platinum crucible, add 5 ml of concentrated sulphuric acid and 5 ml of hydrofluoric acid and evaporate to dense white fumes. Cool the crucible and contents, carefully dilute the contents with 5 ml of water and transfer the solution to the filtrate obtained under **23.3.1**. Wash the crucible with water. Complete the estimation as under **10.3.2** to **10.4**.

SECTION IV SILICOMANGANESE

24. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

24.1 Outline of the Method — same as in **14.1**.

24.2 Apparatus — 50-ml iron crucible.

24.3 Reagents — same as under **14.3**.

24.4 Procedure

24.4.1 Weigh accurately 0·5 g of the sample and transfer to a 50-ml iron crucible. Add approximately about 10 g of sodium peroxide and mix the contents thoroughly with a small iron or nickel rod. Cover the mixture with a layer of about 2 g additional sodium peroxide. Carry out baking as under **5.4.2** and **5.4.3** and reserve the filtrate for estimation of manganese by the Bismuthate and Volhard methods (*see* **25** and **26**). Complete the estimation of silicon as given under **5.4.4** to **5.5**.

25. DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD

25.1 Outline of the Method — same as in **19.1**.

25.2 Reagents — same as under **19.2**.

25.3 Procedure

25.3.1 Take the solution reserved under **24.4.1** and evaporate with 10 ml of concentrated sulphuric acid to fumes. Cool, dilute to 100 ml cautiously and boil until all the salts are dissolved. Transfer to a 500-ml flask and make up to the mark. Use suitable aliquots for determination of manganese by the Bismuthate or Volhard methods.

25.3.2 Pipette out exactly 25 ml of the solution (or such portion that will contain 0·03 g of manganese) into a 500-ml beaker and complete the estimation as described under **19.3.2** to **19.4**.

26. DETERMINATION OF MANGANESE BY THE VOLHARD (ALTERNATE) METHOD

26.1 Determine manganese content of the sample by following the procedure as given under **20** with the following modifications.

26.1.1 Pipette out 25 ml of the solution prepared under **25.3.1** and complete the estimation as described under **20.3.1** to **20.4**.

27. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

27.1 Determine carbon content by following the method as described under **7** with the following modifications.

27.1.1 Use one gram of the sample.

27.1.2 Use a furnace temperature between 1 200 to 1 300°C.

28. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

28.1 Determine carbon content of the sample by following the procedure given under **8**.

29. DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

29.1 Determine phosphorus content of the sample by following the procedure as given under **22** with the following modification.

29.1.1 Transfer the sample to a large platinum dish provided with a cover and add 50 ml of concentrated nitric acid and then 10 to 15 ml of hydrofluoric acid in small amounts. Complete the estimation as under **23.3.1** and **23.3.2**.

30. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

30.1 Determine sulphur content of the sample by following the procedure as given under **9**.

SECTION V FERROMOLYBDENUM

31. DETERMINATION OF MOLYBDENUM BY THE PERMANGANATE TITRATION METHOD

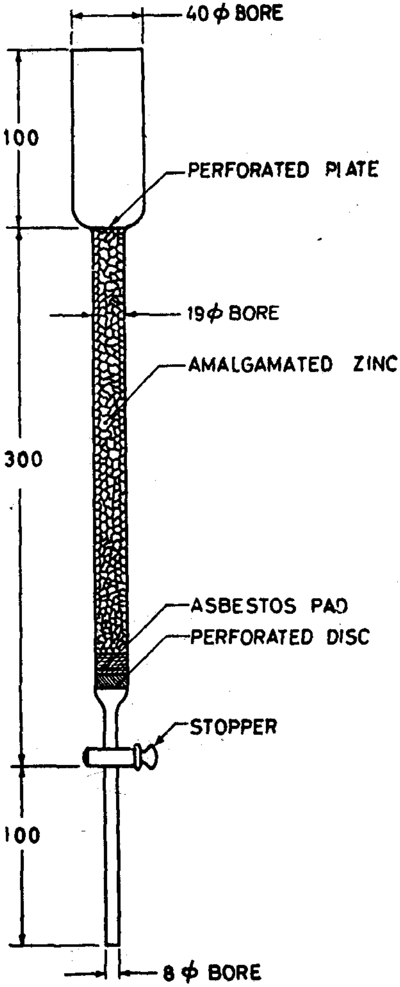
31.1 Outline of the Method — After the removal of silica and iron, the latter having been removed by repeated precipitation, molybdenum is separated from the ammoniacal filtrate by treatment with hydrogen sulphide in presence of tartaric acid and reduced in a Jones reductor provided with ferric sulphate solution in the receiver. The reduced solution is then titrated with standard potassium permanganate solution in presence of phosphoric acid.

31.2 Apparatus

31.2.1 *Jones Reductor* — conforming to the dimensions shown in Fig. 4.

31.3 Reagents

31.3.1 *Dilute Nitric Acid* — 1 : 3 (*v/v*).



All dimensions in millimetres.

Fig. 4 Jones Reductor

31.3.2 *Hydrofluoric Acid* — 40 percent.

31.3.3 *Dilute Sulphuric Acid* — 1 : 1 , 1 : 4, 5 : 95 and 3 : 97 (*v/v*).

31.3.4 *Dilute Ammonium Hydroxide* — 1 : 3 and 1 : 5 (*v/v*).

31.3.5 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

31.3.6 *Tartaric Acid* — solid.

31.3.7 *Hydrogen Sulphide* — gas.

31.3.8 *Ammonium Sulphide Wash Solution* — Saturate ammonium hydroxide (1 : 99) with hydrogen sulphide.

31.3.9 *Tartaric Acid Wash Solution* — Dissolve 10 g of tartaric acid in one litre of dilute sulphuric acid (1 : 99) and saturate with hydrogen sulphide gas.

31.3.10 *Concentrated Sulphuric Acid* — *see* **7.3.1**.

31.3.11 *Concentrated Nitric Acid* — *see* **6.3.1**.

31.3.12 *Potassium Permanganate Solution* — 2·5 percent (*w/v*).

31.3.13 *Zinc* (20 *to* 30 *mesh*) — It should not contain more than 0·002 percent of iron.

31.3.14 *Ferric Sulphate Solution* — Dissolve 80 g of ferric sulphate in one litre of dilute sulphuric acid (1 : 4).

31.3.15 *Phosphoric Acid* — 85 percent.

31.3.16 *Standard Potassium Permanganate Solution* — 0·1 N. *See* **19.2.7**.

31.3.17 *Aluminium Persulphate* — solid.

31.3.18 *Potassium Thiocyanate Solution* — 5 percent (*w/v*).

31.3.19 *Stannous Chloride Solution* — Dissolve 350 g of stannous chloride in 200 ml of dilute hydrochloric acid (1 : 1) in a conical flask. Boil gently until complete solution is obtained. Dilute the solution to one litre, add two pieces of metallic tin and stopper the flask.

31.3.20 *Isopropyl Ether*

31.3.21 *Standard Molybdenum Solution* (1 ml = 0·000 5 g of Mo) — Dissolve 1·25 g of pure sodium molybdate ($Na_2MoO_4, 2H_2O$) in one litre of water containing 5 ml of concentrated sulphuric acid. Standardize against standard potassium permanganate solution as described under **31.4.5**.

31.4 Procedure

31.4.1 Transfer 0·5 g of the sample to a 150-ml beaker, add 10 ml of dilute nitric acid, cover and warm to complete solution. One or two drops of hydrofluoric acid may be added if any difficulty in getting complete solution is experienced. When the reaction is complete, add 10 ml of dilute sulphuric acid (1 : 1) cautiously, and evaporate to dense white fumes. Cool and add 40 ml of water and warm. Rinse the cover and remove it. Filter and wash the paper and silica 12 to 15 times with hot water, three to four times with dilute ammonium hydroxide (1 : 3) and finally four to five times with hot water. Run the washings into the main filtrate. Discard the precipitate.

31.4.2 Cool the filtrate from **31.4.1**, add concentrated ammonium hydroxide until a permanent red colour is obtained. Heat the acid solution gently to boiling, pour the solution slowly with vigorous stirring into 75 ml of nearly boiling ammonium hydroxide (1 : 5) contained in a 500-ml beaker. Add a little paper pulp and filter into 500-ml beaker. Wash the residue with hot water and preserve the filtrate. Dissolve the precipitate in slight excess of hot dilute sulphuric acid (1 : 4), nearly neutralize with concentrated ammonium hydroxide and then pour into dilute ammonium hydroxide (1 : 5) as described before. Filter into the reserved filtrate and wash the precipitate with hot water. Dissolve the precipitate and repeat the operation. Preserve the combined filtrate.

31.4.3 Treat the combined ammoniacal filtrate obtained under **31.4.2** with 3 g of powdered tartaric acid, stir to dissolve, and saturate the warm solution with hydrogen sulphide. If a precipitate appears, filter and wash with ammonium sulphide wash solution. Warm the filtrate, cover the beaker, and add dilute sulphuric acid (1 : 1) until the solution contains 8 ml of acid in excess for each 100 ml of the solution. At this stage no further effervescence takes place and the odour of ammonium sulphide as well as colour of thiomolybdate has disappeared. If too little acid has been added, some molybdenum may remain in solution. Let the solution stand at the side of a steam-bath (about 40°C) for 15 minutes until the precipitate has settled. Filter and wash the precipitate thoroughly with tartaric acid wash solution. Reserve the filtrate.

31.4.4 Transfer the paper and precipitate to the original 500-ml beaker, cover and treat with 6 ml of concentrated sulphuric acid and 10 ml of concentrated nitric acid. Heat the solution cautiously to dense white fumes. Let it cool, add 5 ml of concentrated nitric acid, again heat to fumes and repeat the treatment until the yellow colour due to organic matter has disappeared. Cool, rinse and remove the cover, rinse the inside of the beaker and again evaporate to fumes. Again cover, cool slightly and add potassium permanganate solution (2·5 percent) very cautiously until a permanent red colour is obtained. Heat to boiling, cool and add 70 ml of water. Boil for a few minutes, add 2 g of zinc and continue boiling until molybdenum has been reduced and any copper present has also been reduced to metallic form. Filter through close texture paper and wash with hot water.

31.4.5 Pass through the Jones reductor, 100 ml of dilute sulphuric acid (5 : 95) and then 50 ml of cold water. Discard the wash solution. Add 30 ml of ferric sulphate solution to the receiver, 5 ml of phosphoric acid and enough water so that the tip of the reductor dips well beneath the surface of the solution. Pass the cooled molybdenum solution containing 5 percent by volume of concentrated sulphuric acid. Shake the receiving flask. Add 50 ml of cold dilute sulphuric acid (3 : 97) just before the level of the molybdenum solution reaches the zinc. Finally rinse with 100 ml of water to wash out all the reduced compound. Close the stop-cock allowing some water to remain in the reductor funnel. Disconnect, raise the reductor, rinse the stem and titrate the solution with standard potassium permanganate solution till pink colour persists.

31.4.6 Make a blank determination following the same procedure and using the same amounts of reagents, but without the material.

31.4.7 Boil the filtrate reserved under **31.4.3** and adjust the volume to 100 ml. Add 1 to 2 g of ammonium persulphate, boil and cool to 15°C. Add sufficient dilute sulphuric acid (1 : 1), so that the solution contains 10 percent by volume of sulphuric acid.

31.4.8 Adjust the temperature to 25°C and transfer it to a 500-ml separating funnel. Add 10 ml of potassium thiocyanate solution and 10 ml of stannous chloride solution. Stopper the funnel and shake vigorously for several minutes. Add about 50 ml of ether and shake vigorously for one to two minutes more. Let stand until the solution has separated with 2 layers. Draw off and set aside the lower layer and transfer the extract to a 100-ml Nessler tube (N_1). Re-extract the lower layer with ether and return the etherial layer, if coloured, to the 100-ml Nessler tube (N_1).

31.4.9 Transfer 25 ml of ferric sulphate solution to a 250-ml separating funnel and add from a burette enough standard molybdenum solution to approximate the molybdenum content of the solution. Dilute to 100 ml with cold water and proceed as described under **31.4.8** until the solution has been transferred to a second 100-ml Nessler tube (N_2).

31.4.10 Allow both the sample solution and the coloured standard solution to stand for several minutes before comparing. Dilute the darker of the two solutions with ether until the colours match approximately. Measure the intensities of colours in a suitable colorimeter or with the help of an absorptiometer.

31.5 Calculation

$$\text{Molybdenum, percent} = \frac{[(A-B)\,C \times 0{\cdot}032] + D}{E} \times 100$$

where

A = volume in ml of the standard permanganate solution required for titration of reduced molybdenum solution,

B = volume in ml of the standard permanganate solution required for the blank,

C = normality of the standard permanganate solution,

D = weight in g of molybdenum determined colorimetrically, and

E = weight in g of the sample taken.

32. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

32.1 Outline of the Method — The sample is decomposed with nitric acid and sulphuric acid and silica in the solution of the sample is estimated by hydrofluorization as usual.

32.2 Reagents — In addition to the reagents given under **5.3**, the following reagents are required.

32.2.1 *Dilute Nitric Acid* — 1 : 3 (*v/v*).

32.2.2 *Dilute Hydrochloric Acid* — 1 : 4.

32.3 Procedure — Transfer one gram of the accurately weighed sample to a porcelain basin and add 10 ml of dilute nitric acid. When the action ceases, add 20 ml of dilute sulphuric acid and evaporate to dense white fumes. Cool, add 75 ml of dilute hydrochloric acid (1 : 4), heat till all soluble salts have dissolved and filter immediately. Wash the filter and the residue with hot dilute hydrochloric acid (1 : 20) and with hot water alternately and finally with hot water till free from chlorides and sulphates. Complete the estimation as described under **5.4.4** to **5.5**.

33. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

33.1 Determine the carbon content of the sample by following the procedure given under **6** with the following modifications.

33.1.1 Use one to two grams of the sample.

33.1.2 Use a furnace temperature of 1 100 to 1 200°C.

34. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

34.1 Determine the carbon content of the sample by following the procedure as given under **8**.

35. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

35.1 Outline of the Method — After the removal of silica from the solution of the sample, sulphur and molybdenum are both precipitated as barium sulphate and barium molybdate respectively, in acidic medium by the addition of barium chloride solution. The precipitate is ignited, fused with sodium carbonate, extracted with water and molybdenum precipitated by α - benzoinoxime solution. Sulphur in the filtrate is precipitated as barium sulphate as before, filtered, ignited and weighed.

35.2 Reagents — In addition to the reagents given under **9.2**, the following reagents are required.

35.2.1 *Sodium Carbonate* — anhydrous.

35.2.2 α - *Benzoinoxime Solution* (*Cupron*) — 2 percent (*w/v*). Dissolve 2 g of α - benzoinoxime in 100 ml of alcohol.

35.2.3 α - *Benzoinoxime Wash Solution* — Dilute 5 ml of the α - benzoinoxime solution (*see* **35.2.2**) to one litre with cold dilute hydrochloric acid (1 : 99).

35.3 Procedure

35.3.1 Transfer in small portions 5 g of the sample to a porcelain vessel containing 50 to 60 ml of concentrated nitric acid and cooled by immersion in ice water. Add 30 ml of concentrated hydrochloric acid and evaporate to dryness. Add 30 ml more of concentrated hydrochloric acid, evaporate to dryness, and bake for 30 minutes at 100 to 110°C. Filter, wash with dilute hydrochloric acid (1 : 99). Evaporate to dryness and bake again for 30 minutes. Take up with 25 to 50 ml of concentrated hydrochloric acid and when solution is complete, dilute with water and filter to remove silica.

35.3.2 Evaporate the filtrate to 15 to 25 ml and dilute to 100 ml with warm water. Add a little paper pulp, filter and wash first with dilute hydrochloric acid (1 : 99) and then with water. Dilute the filtrate to 200 ml and warm at 70 to 80°C, add 20 ml of barium chloride solution dropwise with constant stirring. Allow to stand for two hours at steam-bath and overnight at the room temperature. Filter through Whatman filter paper No. 42 and wash the precipitate as described under **9.3.3**.

35.3.3 Ignite the precipitate in a 30-ml platinum crucible at 500 to 600°C and fuse the residue with 2 to 3 g of sodium carbonate, cool and dissolve the cold melt in 50 ml of hot water. Filter and wash the residue with warm water. Acidify the filtrate with concentrated hydrochloric acid and add 2 ml in excess, cool to 15 to 20°C, add a little ashless paper pulp and sufficient amount (2 to 5 ml) of α - benzoinoxime solution to precipitate molybdenum. Stir well and filter through filter paper No. 540 and wash with cold α - benzoinoxime wash solution. Complete the estimation as described under **9.3.3** to **9.4**.

SECTION VI FERROPHOSPHORUS

36. DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE-MAGNESIA (GRAVIMETRIC) METHOD

36.1 Outline of the Method — After the decomposition of the sample by fusion with sodium peroxide, phosphorus is precipitated from the warm acid solution as ammonium phosphomolybdate, dissolved in ammonia, re-precipitated as magnesium-ammonium phosphate which is finally ignited and weighed as magnesium pyrophosphate.

36.2 Reagents

36.2.1 *Sodium Peroxide* — solid.

36.2.2 *Dilute Nitric Acid* — 1 : 99 (*v*/*v*).

36.2.3 *Potassium Permanganate Solution* — 25 g per litre (*w*/*v*).

36.2.4 *Sulphurous Acid* — Saturate water with sulphur dioxide gas. Prepare fresh as needed.

36.2.5 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

36.2.6 *Concentrated Nitric Acid* — *see* **6.3.1**.

36.2.7 *Ammonium Molybdate Solution* — *see* **10.2.10**.

36.2.8 *Dilute Ammonium Hydroxide* — 1 : 1 and 1 : 20 (*v*/*v*).

36.2.9 *Citric Acid* — solid.

36.2.10 *Concentrated Hydrochloric Acid* — *see* **5.3.3**.

36.2.11 *Magnesia Mixture* — Dissolve 130 g of magnesium sulphate ($MgSO_4, 7H_2O$) and 75 g of ammonium sulphate in 500 ml of water. Add concentrated ammonium hydroxide in slight excess and let stand overnight. Filter, if necessary and make the solution just acidic by adding a very slight excess of concentrated sulphuric acid, dilute to one litre and keep in a glass-stoppered bottle.

36.3 Procedure

36.3.1 Transfer one gram of finely powdered and accurately weighed sample to an iron crucible and mix with 15 g of sodium peroxide. Spread a thin layer of sodium peroxide on the top of the mixture, cover the crucible with iron lid and fuse the contents by heating first at low temperature and then gradually raising the temperature until complete fusion takes place. Rotate the crucible sufficiently to attack any undissolved particle of the alloy sticking along the sides of the crucible and stir up the fused mass. Keep the contents of the crucible in a molten state for about five minutes, then heat to bright redness for a minute and allow to cool.

36.3.2 Place the crucible in a covered beaker containing about 300 ml of water. Warm for few minutes, remove the crucible and wash it well with warm dilute nitric acid. Neutralize the solution by slowly adding dilute nitric acid and add 40 ml in excess and digest until the solution clears. Filter the solution through a tight paper in a 500-ml volumetric flask and wash the residue with warm dilute nitric acid. Cool to 20°C, dilute to exactly 500 ml, mix well and pipette out an aliquot of 100 ml into a 400-ml beaker.

36.3.3 Add 20 ml of dilute nitric acid and 5 to 10 ml of potassium permanganate solution, and carefully boil until manganese is precipitated. If no precipitate appears, add more potassium permanganate solution and boil again. Dissolve the precipitate by adding sulphurous acid dropwise and boil for two minutes. Add a few millilitres more of sulphurous acid and boil off excess sulphurous acid and neutralize the solution with concentrated ammonium hydroxide until a slight precipitate appears. Redissolve the precipitate by the continuous addition of few drops of concentrated nitric acid, add 4 to 5 ml in excess and heat to 70 to 80°C. Add with stirring 80 ml of ammonium molybdate solution; 70 ml for every 0·1 g of phosphorus pentoxide. Continue stirring until the phosphorus is precipitated. Digest at 50 to 60°C for an hour. Cool to room temperature and filter the precipitate on an ashless paper pulp pad, wash the precipitate with cold dilute nitric acid.

36.3.4 Transfer the funnel and the filter pad to the original beaker in which phosphorus was precipitated and wash down the precipitate by the dropwise addition of dilute ammonium hydroxide (1 : 1), finally washing the pad and funnel with hot water. Add 2 g of citric acid and pour the solution through the filter which might contain some yellow precipitate and catch the solution in another 400 ml beaker. Wash the beaker and paper several times with dilute ammonium hydroxide (1 : 20), then with hot water, and then with dilute hydrochloric acid (1 : 20), and finally for several times with dilute ammonium hydroxide (1 : 20). If the solution in the beaker is not clear, heat it to boiling and filter through the same paper. The volume at this juncture should be 150 ml. Neutralize the ammoniacal solution with concentrated hydrochloric acid and add one millilitre of concentrated hydrochloric acid in excess. Add 20 ml of magnesia mixture for every 0·1 g of phosphorus. Add concentrated ammonium hydroxide dropwise and continue stirring until the solution is ammoniacal and most of the phosphorus has been precipitated. Finally add 15 ml of concentrated ammonium hydroxide and allow the solution to stand overnight. Filter, wash the magnesium ammonium phosphate precipitate for several times with dilute ammonium hydroxide (1 : 20) until free from chloride.

36.3.5 Ignite the precipitate carefully in a platinum or silica crucible, at a low temperature until the carbon paper is burnt. Finally ignite to constant weight at 1 000°C and weigh as $Mg_2P_2O_7$.

36.3.6 Make a blank determination using the same procedure and same quantities of reagents, but without the sample.

36.4 Calculation

$$\text{Phosphorus, percent} = \frac{(A-B) \times 27{\cdot}86}{C}$$

where

A = weight in g of the magnesium pyrophosphate precipitate,

B = correction for the blank, and

C = weight in g of the sample represented by the aliquot used.

37. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

37.1 Determine the carbon content of the sample by following the procedure given under **6** with the following modifications.

37.1.1 Use one to two grams of the sample.

37.1.2 Use a furnace temperature of 1 100 to 1 200°C.

38. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

38.1 Determine the carbon content of the sample by following the procedure as given under **8**.

SECTION VII FERROTITANIUM

39. DETERMINATION OF TITANIUM BY THE CUPFERRON (GRAVIMETRIC) METHOD

39.1 Outline of the Method — After attacking the sample with sulphuric acid, nitric acid and hydrofluoric acid, hydrogen sulphide separations in acid and alkali media are made. Titanium is then precipitated with cupferron, ignited and weighed as oxide. Corrections for vanadium and zirconium, if present, are made.

39.2 Reagents

39.2.1 *Dilute Sulphuric Acid* — 1 : 1, 1 : 4 and 1 : 9 (*v*/*v*).

39.2.2 *Hydrofluoric Acid* — 40 percent.

39.2.3 *Concentrated Nitric Acid* — *see* **6.3.1**.

39.2.4 *Tartaric Acid Solution* — 500 g/l. Dissolve 500 g of tartaric acid in water and dilute to one litre.

39.2.5 *Hydrogen Sulphide* — gas.

39.2.6 *Hydrogen Sulphide Wash Solution* — Add 20 ml of dilute sulphuric acid (1 : 1) to 20 ml of tartaric acid solution (*see* **39.2.4**) and dilute the solution to one litre. Saturate it with hydrogen sulphide gas.

39.2.7 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

39.2.8 *Ammonium Sulphide Wash Solution* — Dissolve 20 g of ammonium chloride and 10 g of ammonium tartarate in 500 ml of water. Add ammonium hydroxide in slight excess, dilute to one litre and saturate with hydrogen sulphide gas.

39.2.9 *Cupferron Solution* — 6 percent. Dissolve 6 g of cupferron in 80 ml of cold water, dilute to 100 ml and filter through filter paper No. 1. Prepare fresh as required.

39.2.10 *Cupferron Wash Solution* — Dilute 20 ml of cupferron solution (*see* **39.2.9**) to one litre with cold dilute sulphuric acid (1 : 9).

39.2.11 *Potassium Bisulphate* — solid.

39.2.12 *Hydrogen Peroxide* — 20 volumes.

39.2.13 *Ammonium Phosphate Solution* — Dissolve 160 g of diammonium hydrogen phosphate in water and dilute to one litre. Filter before use.

39.2.14 *Concentrated Sulphuric Acid — see 7.3.1.*

39.2.15 *Perchloric Acid* — 70 percent.

39.2.16 *Phosphoric Acid* — 85 percent.

39.3 Procedure

39.3.1 Transfer 0·5 g of the accurately weighed sample to a 100-ml platinum dish. Cover and add 15 ml of dilute sulphuric acid (1 : 1), 5 ml of hydrofluoric acid (10 ml of the acid shall be taken, if silicon is over 10 percent) and sufficient concentrated nitric acid dropwise to effect dissolution. Remove and rinse the cover and sides of the dish. Evaporate to fumes of sulphuric acid and cool. Add 30 ml of dilute sulphuric acid (1 : 4), stir well, heat for a few minutes and transfer to a 400-ml beaker. Heat until all sulphates have dissolved, dilute to 200 ml, add 20 ml of tartaric acid solution and pass a brisk current of hydrogen sulphide for at least 20 minutes.

39.3.2 If a precipitate forms, filter through a paper containing paper pulp, into a 600-ml beaker. Wash about 20 times with hydrogen sulphide wash solution. To the filtrate, or to the clear solution if filtration was unnecessary, add paper pulp and make alkaline by adding concentrated ammonium hydroxide in slight excess. Pass a brisk current of hydrogen sulphide through the solution for at least 7 minutes and filter as soon as the precipitate settles, through a medium paper containing paper pulp, into a 800-ml beaker. Wash the paper and the precipitate about 20 times with ammonium sulphide wash solution. Preserve the paper and the precipitate.

39.3.3 Boil the filtrate for about 10 minutes, then add 25 ml of dilute sulphuric acid (1 : 1) and boil down to 150 ml. Cool to 15 to 20°C, then add a little paper pulp and a slight excess of a cold, freshly prepared cupferron solution. Stir well and filter on two super-imposed medium papers containing a little paper pulp and supported in a Buchner funnel, using moderate suction. Wash about 20 times with cold cupferron wash solution. Preserve the filtrate for the estimation of aluminium.

39.3.4 Ignite the paper and the precipitate in a weighed platinum dish, first at a low temperature to burn off carbonaceous matter and finally at 1 050 to 1 150°C for 20 minutes. Cool and weigh as titanium dioxide. The ignited residue may contain oxides of vanadium and zirconium, and therefore their weight shall be deducted from the weight of impure titanium dioxide. In a separate sample, vanadium shall be determined colorimetrically using hydrogen peroxide, suppressing the titanium colour with hydrofluoric acid. For the determination of zirconium fresh sample shall be fused with potassium bisulphate, the melt taken up with dilute sulphuric acid (1 : 9) and zirconium precipitated as phosphate by adding hydrogen peroxide and ammonium phosphate to the solution.

39.3.5 Return the paper and the precipitate of ferrous sulphide (reserved under **39.3.2**) to the beaker. Add 25 ml of concentrated nitric acid, and 10 ml each of concentrated sulphuric acid and phosphoric acid. Evaporate to dense white fumes to destroy all organic matter. Add 100 ml of water and digest until salts are in solution.

Transfer to a 200-ml volumetric flask, dilute to the mark and mix thoroughly. Determine the titanium content by developing colour with hydrogen peroxide and measuring the intensity of colour in a suitable colorimeter.

39.4 Calculation

$$\text{Titanium, percent} = \frac{(A \times 0{\cdot}599\,5) + B}{C} \times 100$$

where

A = corrected weight in g of titanium dioxide,

B = weight in g of titanium from ferrous sulphide precipitate (*see* **39.3.5**), and

C = weight in g of the sample taken.

40. DETERMINATION OF ALUMINIUM BY THE PHOSPHATE METHOD

40.1 Outline of the Method — The filtrate from the titanium determination (*see* **39.3.3**) is treated with nitric acid and sulphuric acid and the aluminium precipitated as phosphate.

40.2 Reagents — same as given under **11.2** and **39.2**.

40.3 Procedure — Take the filtrate reserved under **39.3.3** and add **20 ml** of concentrated nitric acid and boil. After the cupferron has been destroyed, add 5 ml of concentrated sulphuric acid and evaporate to dense white fumes. Cool, add 150 ml of water. Heat to boiling and add 10 ml of ammonium phosphate solution. Further complete the estimation as under **11.3.4** to **11.4**.

41. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

41.1 Outline of the Method — The sample is fused with sodium peroxide, the melt dissolved in sulphuric acid and the solution evaporated to dense white fumes to dehydrate the silica which is estimated by hydrofluorization as usual.

41.2 Reagents — In addition to the reagents given under **5.3**, the following reagents are required.

41.2.1 *Sodium Peroxide* — solid.

41.2.2 *Dilute Sulphuric Acid* — 1 : 200 (*v*/*v*).

41.2.3 *Oxalic Acid Solution* — 100 g/l. Dissolve 100 g of oxalic acid in water and dilute to one litre.

41.3 Procedure

41.3.1 Mix 0·5 g of the accurately weighed sample, for silicon in the ~~2 to~~ 15 percent range, or 0·25 g of the sample for silicon in 15 to 25 percent range, in an iron crucible with 8 to 10 g of dry sodium peroxide as under **14.4.1**.

41.3.2 Transfer the cold cake to a dry 500-ml casserole, dissolve in water, cover and add 80 ml of dilute sulphuric acid (1 : 1). Rinse the crucible thoroughly with hot water, adding the washings to the *casserole. Add 50 ml of oxalic acid solution and evaporate slowly to fumes.

41.3.3 Heat to dense white fumes and continue the fuming for 3 to 5 minutes, cool, add 200 ml of warm water, heat to dissolve sulphates. Filter through filter paper No. 40 into a 500-ml casserole and wash at least 20 times with hot dilute sulphuric acid (1 : 200). Further complete the estimation as described under **5.4.4** to **5.5**.

42. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

42.1 Determine the carbon content of the sample by following the procedure as given under **33**.

SECTION VIII FERROVANADIUM

43. DETERMINATION OF VANADIUM BY THE PERMANGANATE TITRATION METHOD

43.1 Outline of the Method — Vanadium in the sulphuric acid-nitric acid solution of the sample is oxidized to vanadic acid and then reduced by slight excess of ferrous solution, the excess of which is destroyed by ammonium persulphate, reduced vanadium is then titrated with standard permanganate solution.

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*As the solution approaches the fuming point, bumping is likely to occur unless oxalic acid has been added which serves as an anti-bumping agent; some foaming occurs as the fuming point is reached but it does not harm.

43.2 Reagents

43.2.1 *Sulphuric Acid-Nitric Acid Mixture* — Mix two volumes of dilute sulphuric acid (1 : 3) with one volume of dilute nitric acid (1 : 1).

43.2.2 *Hydrofluoric Acid* — 40 percent.

43.2.3 *Standard Potassium Permanganate Solution* — 0·1 N. *See* **19.2.7**.

43.2.4 *Ferrous Ammonium Sulphate Solution* — 0·1 N approximately. *See* **19.2.5**.

43.2.5 *Potassium Ferricyanide Indicator Solution* — Dissolve 0·1 g of the reagent in 100 ml of water. Prepare fresh as needed.

43.2.6 *Ammonium Persulphate Solution (95 percent pure)* — 15 percent (*w/v*). Prepare fresh as needed.

43.3 Procedure

43.3.1 Transfer 0·25 to 0·5 g of the sample to a 600-ml beaker and add 80 ml of sulphuric acid-nitric acid mixture. If the silica content is high and the alloy fails to decompose completely, add a few millilitres of hydrofluoric acid substituting beaker with 200-ml platinum dish. After the reaction is over, evaporate the solution to dense white fumes. Cool, add 100 ml of water and heat until salts are dissolved.

43.3.2 Transfer the solution to a 800-ml beaker, dilute to 400 ml and to the cooled solution add standard potassium permanganate solution until a strong pink colour has developed that persists for 30 seconds. Cool the solution to 15°C and reduce vanadium by adding ferrous ammonium sulphate solution till the presence of ferrous iron is indicated by the ferricyanide spot test (tested externally). Add 5 ml of ferrous ammonium sulphate solution in excess and stir the solution for at least one minute. Cool to 15°C and oxidize the excess ferrous iron with 8 to 10 ml of ammonium persulphate solution. Stir the solution vigorously for one minute. Titrate the solution with standard potassium permanganate solution until a faint pink colour appears and persists for 30 seconds.

43.4 Calculation

$$\text{Vanadium, percent} = \frac{A\,B \times 5{\cdot}095}{C}$$

where

A = volume in ml of the standard potassium permanganate solution required for the titration,

B = normality of the standard potassium permanganate solution, and

C = weight in g of the sample taken.

44. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

44.1 Outline of the Method — The sample is dissolved in sulphuric acid-nitric acid mixture or in case of high-silicon alloy, fused with sodium peroxide and extracted with sulphuric acid. The solution is fumed to dehydrate silica and filtered. Silica is then hydrofluorized and estimated as usual.

44.2 Reagents — In addition to the reagents given under **5.3** the following reagents are required:

44.2.1 *Sulphuric Acid-Nitric Acid Mixture* — Slowly stir 160 ml of concentrated sulphuric acid (*see* **7.3.1**) in 660 ml of water and add 180 ml of concentrated nitric acid (*see* **9.2.1**).

44.2.2 *Sodium Peroxide* — solid.

44.2.3 *Potassium Bisulphate* — solid.

44.3 Procedure

44.3.1 Dissolve 2 g of the accurately weighed sample of low-silicon alloy in 40 ml of sulphuric acid-nitric acid mixture in a platinum dish and evaporate to dense white fumes.

44.3.2 In case of high-silicon alloy fuse one gram of the accurately weighed sample with 8 g of sodium peroxide in 30-ml iron crucible as described under **14.4.1**. Extract the melt, with caution, with 80 ml of dilute sulphuric acid in a porcelain casserole. Evaporate the solution to dense white fumes.

44.3.3 Cool, add 125 ml of water and heat for a few minutes, stirring frequently, until all salts are dissolved. Immediately filter and wash the precipitate with hot dilute hydrochloric acid (1 : 20) and hot water alternately to complete the removal of iron salts and finally wash with hot water until free from acid. Preserve the filtrate for the estimation of phosphorus and further complete the estimation as described under **5.3.3** to **5.5**.

44.3.4 Fuse the residue after hydrofluorization in the platinum crucible with potassium bisulphate, extract the melt with water and add it to the main filtrate reserved in **44.3.3** for the estimation of phosphorus.

45. DETERMINATION OF ALUMINIUM BY THE CUPFERRON-PHOSPHATE METHOD

45.1 Outline of the Method — From the sulphuric acid-nitric acid solution of the sample, vanadium and iron are separated by double precipitation with cupferron. Aluminium in the filtrate is precipitated as hydroxide, dissolved in hydrochloric acid converted to phosphate in an alkaline medium, and weighed as aluminium phosphate.

45.2 Reagents

45.2.1 *Dilute Sulphuric Acid* — 1 : 2 (*v*/*v*).

45.2.2 *Concentrated Nitric Acid* — *see* **6.3.1**.

45.2.3 *Hydrofluoric Acid* — 40 percent.

45.2.4 *Potassium Permanganate Solution* — 25 g/l.

45.2.5 *Cupferron Solution* — *see* **39.2.9**.

45.2.6 *Cupferron Wash Solution* — *see* **39.2.10**.

45.2.7 *Concentrated Sulphuric Acid* — *see* **7.3.1**.

45.2.8 *Ammonium Chloride* — solid.

45.2.9 *Bromocresol Purple Indicator Solution* — *see* **40.2.16**.

45.2.10 *Dilute Ammonium Hydroxide* — 1 : 1 (*v*/*v*).

45.2.11 *Ammonium Chloride Solution* — 20 g/l.

45.2.12 *Dilute Hydrochloric Acid* — 1 : 3 and 1 : 9 (*v*/*v*).

45.2.13 *Diammonium Hydrogen Phosphate* — solid.

45.2.14 *Methyl Red Indicator* — Dissolve 0·1 g of methyl red in 372 ml of 0·1 N sodium hydroxide and dilute to 250 ml with water. Filter, if necessary.

45.2.15 *Ammonium Acetate Solution* — 200 g/l.

45.2.16 *Ammonium Nitrate Solution* — 50 g/l.

45.3 Procedure

45.3.1 Decompose one gram of the sample with 60 ml of dilute sulphuric acid and 10 ml of concentrated nitric acid in a platinum dish. Add 2 to 3 ml of hydrofluoric acid and evaporate to dense white fumes. Cool a little, add water and heat to dissolve salts. Transfer to a 400-ml beaker and add potassium permanganate solution till a pink colour persists. Dilute to 100 ml and cool to 5 to 10°C. Add some ashless paper pulp and precipitate iron and vanadium by adding cupferron solution until an excess of the reagent is shown by the appearance of a white curdy precipitate instead of the brown one formed first. Stir vigorously for 2 to 3 minutes and filter through filter paper No. 41. Wash thoroughly with cupferron wash solution. Reserve the filtrate.

45.3.2 Return the precipitate to the original beaker and add 10 ml of concentrated sulphuric acid and 50 ml of concentrated nitric acid and evaporate to fumes. Add more concentrated nitric acid, if necessary, and repeat the evaporation to oxidize all organic matter. Cool, add 100 ml of water and digest until all salts are in solution. Cool to 5 to 10°C, add an excess of potassium permanganate and re-precipitate with cupferron solution. Filter and wash as in **45.3.1**. Combine this filtrate with that reserved in **45.3.1**.

45.3.3 To the combined filtrate, add 75 ml of concentrated nitric acid and evaporate to fumes. Add concentrated nitric acid again, if necessary, and evaporate to fumes to oxidize all organic matter. Cool, dilute with 100 ml water, add 10 g ammonium chloride and a few drops of bromocresol purple indicator solution. Add dilute ammonium hydroxide until the solution just turns purple. Boil the solution for one minute, allow to settle, filter and wash with warm ammonium chloride solution. Dissolve the precipitate in 50 ml of hot dilute hydrochloric acid (1 : 3) and repeat the precipitation with ammonia as before. Dissolve the precipitate on the paper with 50 ml of hot dilute hydrochloric acid (1 : 3) and wash the paper with hot water.

45.3.4 To the filtrate and washings, add 0·5 g of diammonium hydrogen phosphate, a little ashless paper pulp and two drops of methyl red indicator and make just ammoniacal. Restore the pink colour by adding dilute hydrochloric acid (1 : 9) drop by drop. Heat the solution to boiling and add 20 ml of ammonium acetate solution. Continue the boiling for 5 minutes, allow to settle, filter and wash with hot ammonium nitrate solution till free from chlorides. Ignite in a porcelain crucible to constant weight at 950 to 1 000°C. Weigh as aluminium phosphate.

45.3.5 Make a blank determination following the same procedure and using the same amounts of reagents but without the material.

45.4 Calculation

$$\text{Aluminium, percent} = \frac{(A-B) \times 22{\cdot}1}{C}$$

where

A = weight in g of aluminium phosphate obtained,

B = correction for blank in g, and

C = weight in g of the sample taken.

46. DETERMINATION OF PHOSPHORUS BY THE ALKALI METRIC METHOD

46.1 Determine phosphorus content of the sample by following the procedure as given under **10** with the following modification.

46.1.1 Dilute the filtrate reserved under **44.3.4** to about 200 ml, heat to boiling and add potassium permanganate solution until a pink colour persists during 5 minutes boiling. Further complete the estimation as under **10.3.3** to **10.4**.

47. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

47.1 Outline of the Method — After removal of silica, from the nitric acid solution of the sample, followed by the recovery of sulphur from the silica residue, sulphur is precipitated from the reduced solution as barium sulphate, traces of barium vanadate are removed by reprecipitation and then barium sulphate is ignited and weighed.

47.2 Reagents — In addition to the reagents mentioned under **9.2**, the following reagents are required.

47.2.1 *Dilute Hydrochloric Acid* — 3 : 97 (*v*/*v*).

47.2.2 *Sodium Carbonate* — anhydrous.

47.3 Procedure

47.3.1 Transfer 5 g of the sample to a large platinum dish and dissolve in 50 to 60 ml of concentrated nitric acid. Since the reaction is likely to be very rapid, the transfer of the sample is best done in small portions while keeping the dish cooled in ice water. In the case of high silicon alloys, add a few millilitres of hydrofluoric acid, warm if necessary, to complete the reaction. Add 30 ml of concentrated hydrochloric acid and one gram of sodium carbonate and evaporate to dryness on the steam-bath. Add 30 ml more of concentrated hydrochloric acid and again evaporate to dryness and bake for 30 minutes at 100 to 110°C. Moisten the residue with 30 ml concentrated hydrochloric acid and 25 ml of water, heat to dissolve salts and filter through filter paper No. 40 washing the paper and residue with dilute hydrochloric acid (3 : 97). Reserve the filtrate.

47.3.2 Ignite the paper and the residue in a platinum crucible, evaporate to dryness with a few millilitres of hydrofluoric acid and fuse with sodium carbonate. Extract the melt with water, filter and add the filtrate to that reserved in **47.3.1**.

47.3.3 Evaporate the combined filtrate to syrupy consistency. Add 10 ml of concentrated hydrochloric acid, 25 ml of water and 4 to 5 g of zinc, and warm on a steam-bath until iron is reduced to the ferrous state. Filter off the undissolved zinc and wash with dilute hydrochloric acid. Dilute to 200 ml with dilute hydrochloric acid, warm to 50 to 60°C and add 25 ml of barium chloride solution. Stir well and let stand at room temperature overnight.

47.3.4 Filter, with as little transfer of precipitate as possible, through filter paper No. 42, wash the paper two to three times with cold dilute hydrochloric acid and then with warm water. Ignite the paper and contents in a platinum crucible and dissolve the ignited residue in 5 ml of dilute hydrochloric acid and transfer the solution to the original beaker containing most of the barium sulphate. Digest the combined portions so as to dissolve any barium vanadate. Complete the estimation as described under **9.3.3** to **9.4**.

48. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

48.1 Determine the carbon content of the sample by following the procedure as given under **7** with the following modifications.

48.1.1 Use one to two grams of the sample.

48.1.2 Use a furnace temperature of 1 100 to 1 200°C.

49. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

49.1 Determine the carbon content of the sample by following the procedure as given under **8**.

SECTION IX FERROTUNGSTEN

50. DETERMINATION OF TUNGSTEN BY THE ACID DIGESTION-CINCHONINE (GRAVIMETRIC) METHOD

50.1 Outline of the Method — Tungsten is precipitated with cinchonine solution and the last traces recovered from the filtrate by α-benzoinoxime. The precipitate is filtered, washed and ignited to constant weight. The impurities in tungsten are removed by fusion with sodium carbonate.

50.2 Reagents

50.2.1 *Hydrofluoric Acid* — 40 percent.

50.2.2 *Concentrated Nitric Acid — see* **6.3.1**.

50.2.3 *Dilute Sulphuric Acid* — 1 : 1 (*v*/*v*).

50.2.4 *Dilute Ammonium Hydroxide* — 1 : 1 (*v*/*v*).

50.2.5 *Dilute Hydrochloric Acid* — 1 : 1 and 1 : 99 (*v*/*v*).

50.2.6 *Concentrated Hydrochloric Acid — see* **5.3.3**.

50.2.7 *α-Benzoinoxime Solution* — 30 g/l. Dissolve 3 g of α-benzoinoxime in 95 ml of acetone and 5 ml of cold water, filter, if necessary.

50.2.8 *Cinchonine Solution* — Dissolve 125 g cinchonine in one litre of dilute hydrochloric acid (1 : 1).

50.2.9 *Cinchonine — α-Benzoinoxime Wash Solution* — Dilute a mixture of 30 ml of cinchonine solution and 5 ml of α-benzoinoxime to one litre with water.

50.2.10 *Sodium Carbonate* — anhydrous.

50.2.11 *Tartaric Acid* — solid.

50.2.12 *Hydrogen Sulphide* — gas.

50.2.13 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

50.3 Procedure

50.3.1 Transfer one gram of the sample ground to pass IS Sieve 15 to a covered platinum dish, add 5 ml of hydrofluoric acid and add concentrated nitric acid drop by drop while heating, until the sample is dissolved. Remove and rinse the cover, add 15 ml of dilute sulphuric acid and heat cautiously on a sand bath to dense white fumes.

50.3.2 Allow to cool, transfer the residue to a beaker with water, finally wipe the dish with a piece of ashless filter paper and add the paper to the solution. Rinse the dish twice with a little warm dilute ammonium hydroxide, some water and then with a few millilitres of dilute hydrochloric acid and add to the main solution. Dilute the contents of the beaker to about 150 ml, add 10 ml of concentrated hydrochloric acid and boil for five minutes. Remove from the source of heat, dilute to 450 ml with water and add 10 ml of cinchonine solution. Keep overnight at room temperature and add 5 ml of α-benzoinoxime solution. Stir vigorously for several minutes and filter on an ashless paper pulp. Wash thoroughly with cinchonine — α-benzoinoxime wash solution and finally several times with cold dilute hydrochloric acid.

50.3.3 Ignite the residue gently in a weighed platinum crucible. Add a few drops of concentrated nitric acid, dry on water bath and re-ignite at not more than 850°C to constant weight.

50.3.4 Fuse the residue with sodium carbonate and dissolve the fused mass in hot water containing a little alcohol, and filter. Wash the residue thoroughly with hot water. Repeat the fusion of the residue with sodium carbonate as before. Combine the filtrates of two fusions and preserve the combined filtrate. Ignite the paper and the residue, add one or two drops of concentrated sulphuric acid and one millilitre of hydrofluoric acid, evaporate to dryness and ignite again to constant weight.

50.3.5 Acidify the combined filtrate reserved under **50.3.4** with dilute sulphuric acid and add 8 ml of the acid in excess for each 100 ml of the solution. Add few grams of tartaric acid. Warm the solution and saturate it with hydrogen sulphide gas. If *molybdenum* is indicated, filter the precipitate and dissolve in concentrated ammonium hydroxide. Determine the molybdenum content of the solution colorimetrically (*see* **31.4.7** to **31.4.10**).

50.3.6 Determine the amount of insoluble residue in the same weight of sodium carbonate as was used in the test (*see* **50.3.4**).

50.4 Calculation

$$\text{Tungsten, percent} = \frac{[A - (B - C)] \times 79{\cdot}3}{D} - F$$

where

A = weight in g of the impure tungstic oxide (WO_3) obtained under **50.3.3**,

B = weight in g of the insoluble residue obtained from sodium carbonate fusion (*see* **50.3.4**),

C = weight in g of insoluble residue obtained from sodium carbonate used (*see* **50.3.6**),

D = weight in g of the sample used, and

E = molybdenum oxide (MoO_3) percent as determined colorimetrically under **50.3.5**.

51. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

51.1 The carbon content of the sample shall be determined by following the procedure as given under **6** with the following modifications.

51.1.1 Use one to two grams of the sample.

51.1.2 Use a furnace temperature of 1 100 to 1 200°C.

52. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

52.1 Determine the carbon content of the sample by following the procedure given under **8** with following modification.

52.1.1 Use 0·5 g of the sample.

53. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

53.1 Outline of the Method — The sample is fused with sodium peroxide, extracted with water and silica dehydrated by means of sulphuric acid in presence of phosphoric acid which keeps tungsten in solution. Iron is dissolved by the addition of tartaric acid and the silica is filtered, ignited and hydrofluorized as usual.

53.2 Reagents — In addition to the reagents given under **5.3** the following reagents are required.

53.2.1 *Sodium Peroxide* — solid.

53.2.2 *Phosphoric Acid* — 85 percent.

53.2.3 *Perchloric Acid* — 70 percent.

53.2.4 *Tartaric Acid Solutions* — 5 and 8 percent (*w*/*v*).

53.3 Procedure

53.3.1 Fuse one gram of the sample with 10 g of dry sodium peroxide as under **14.4.1**.

53.3.2 Cool and extract in a covered 600-ml tall-form beaker containing 50 ml of water. Remove the crucible, wash thoroughly with water and acidify with 80 ml of dilute sulphuric acid. Transfer the contents of the beaker to a porcelain dish, add 5 ml of phosphoric acid and 10 ml of perchloric acid, evaporate to dense white fumes.

53.3.3 Allow to cool a little and add 200 ml of warm tartaric acid solution (8 percent). Heat at a temperature of 60 to 70°C while stirring occasionally until all ferric sulphate has dissolved. Filter and wash thoroughly with tartaric acid solution (5 percent). Complete the estimation as described under **5.4.4** to **5.5**.

54. DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD

54.1 Outline of the Method — The sample is decomposed with nitric acid and hydrofluoric acid, evaporated to fumes with sulphuric acid. Tungstic acid is separated and the manganese recovered from the residue. The bivalent manganese in the solution is then oxidized to permanganic acid and estimated as usual.

54.2 Reagents — In addition to the reagents given under **19.2** the following reagents are required.

54.2.1 *Concentrated Nitric Acid — see* **6.3.1**.

54.2.2 *Hydrofluoric Acid* — 40 percent.

54.2.3 *Sodium Hydroxide Solution* — 10 percent (*w/v*).

54.2.4 *Standard Ferrous Ammonium Sulphate Solution* — 0·03 N. Dissolve 12 g of ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4)_2, 6H_2O$] in cold dilute sulphuric acid (5 : 95) and make up to one litre with this acid. Mix well and keep in an amber-coloured glass-stoppered bottle.

54.2.5 *Dilute Sulphuric Acid* — 1 : 1 (*v/v*).

54.2.6 *Standard Potassium Permanganate Solution* — 0·03 N. Dissolve 0·958 g of potassium permanganate in water and dilute to one litre. Put the solution aside for two weeks in a dark place, filter without washing through a fritted glass crucible and store in a dark-coloured stoppered bottle. Standardize the permanganate solution against standard sodium oxalate solution (0·03 N). Analyse standard steel of known manganese content to check up the strength of the standard permanganate solution.

54.3 Procedure

54.3.1 Dissolve one gram of the sample in 15 ml of concentrated nitric acid and 5 ml of hydrofluoric acid in a platinum dish. Add 5 ml of concentrated sulphuric acid and evaporate to dense white fumes. Cool and add 50 ml of water. Heat to 80 to 90°C ~~for~~ 15 minutes, while stirring occasionally, and filter into a 300-ml Erlenmeyer flask. Preserve the filtrate.

54.3.2 Place the filter and precipitate into a 250-ml beaker, add 50 ml of sodium hydroxide solution and boil for 5 minutes. Dilute to about 100 ml and filter through filter paper No. 541, washing six times with hot water. Reject the filtrate and washings. Dissolve the residue on the paper with hot dilute sulphuric acid and a few drops of sulphurous acid. Boil off the sulphurous acid, add the solution to the filtrate reserved under **54.3.1** and add 75 ml of concentrated nitric acid. Complete the estimation as described under **19.3.2** to **19.4** with the exception that potassium permanganate and ferrous ammonium sulphate solutions used shall be 0·03 N.

55. DETERMINATION OF MANGANESE BY THE PERSULPHATE-ARSENITE (ALTERNATE) METHOD

55.1 Outline of the Method — After the separation of tungstic acid, manganese, in the solution of the sample, is oxidized with potassium persulphate in presence of silver nitrate and titrated rapidly with sodium arsenite solution.

55.2 Reagents — In addition to the reagents given under **54.2**, the following reagents are required.

55.2.1 *Silver Nitrate Solution* — one percent (*w/v*).

55.2.2 *Ammonium Persulphate Solution* — 25 percent (*w/v*). Prepare fresh as needed.

55.2.3 *Sodium Arsenite (Stock) Solution* — To 15 g of arsenous oxide in a 500-ml flask, add 45 g of sodium carbonate and 150 ml of distilled water. Heat the flask and contents on the steam bath until the arsenous oxide is dissolved. Cool the solution, filter and make up to one litre with distilled water.

55.2.4 *Standard Sodium Arsenite Solution* — Mix 200 ml of the sodium arsenite (stock) solution with 2 500 ml of distilled water and standardize against potassium permanganate 0·01 N or a standard manganese alloy containing about one percent manganese, by dissolving 0·2 g of the latter in 30 ml of mixed acids (200 ml water, 400 ml of concentrated sulphuric acid and concentrated nitric acid).

55.3 Procedure

55.3.1 Dissolve one gram of the sample as described under **54.3.1** and **53.3.2**. Add 100 ml of hot water, 10 ml of ~~silver nitrate solution,~~ 10 ml of ammonium persulphate solution and 5 ml of phosphoric acid. Heat to boiling and boil briskly for one to two minutes. Add 75 ml of water to the solution, cool to about 30°C and titrate rapidly with standard sodium arsenite solution to a clear yellow end point that remains unchanged on further addition of the standard arsenite solution. If the solution is not titrated rapidly, part of the manganese may be reoxidized by the ammonium persulphate during the titration and thus yield high results.

55.4 Calculation

$$\text{Manganese percent} = \frac{AB}{C} \times 100$$

where

A = volume in ml of the standard sodium arsenite solution required to titrate the sample,

B = manganese equivalent of the sodium arsenite solution in g per ml as determined, and

C = weight in g of the sample taken.

56. DETERMINATION OF TIN BY THE IODIMETRIC METHOD

56.1 Outline of the Method — The solution of the sample is made in nitric acid and hydrofluoric acid. Copper, tin, antimony, etc, are precipitated as sulphides with hydrogen sulphide treatment in acid medium. Tin, alongwith arsenic and antimony, is separated, dissolved in hydrochloric acid and potassium chlorate and antimony precipitated by passing hydrogen sulphide through the solution in presence of oxalic acid. Tin in the solution is then reduced to stannous chloride and titrated against potassium iodate in presence of sodium bicarbonate.

56.2 Apparatus — The apparatus for the reduction of tin as shown in Fig. 5 shall be used.

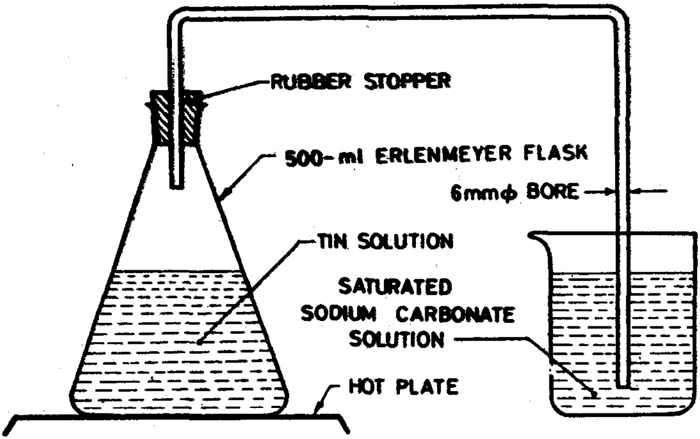

FIG. 5 APPARATUS FOR REDUCTION OF TIN

56.3 Reagents

56.3.1 *Concentrated Nitric Acid — see* **6.3.1**.

56.3.2 *Hydrofluoric Acid* — 40 percent.

56.3.3 *Concentrated Sulphuric Acid* — *see* **7.3.1**.

56.3.4 *Dilute Ammonium Hydroxide* — 1 : 1 (*v*/*v*).

56.3.5 *Dilute Sulphuric Acid* — 1 : 1 (*v*/*v*).

56.3.6 *Tartaric Acid* — solid.

56.3.7 *Concentrated Ammonium Hydroxide* — sp gr 0·90.

56.3.8 *Hydrogen Sulphide* — gas.

56.3.9 *Tartaric Acid Wash Solution* — Dissolve 10 g of tartaric acid in one litre of dilute sulphuric acid (1 : 99) and saturate with hydrogen sulphide gas.

56.3.10 *Potassium Hydroxide — Potassium Sulphide Solution* — Saturate 250 ml of potassium hydroxide (100 g/l) with hydrogen sulphide gas and then add 750 ml of potassium hydroxide (100 g/l).

56.3.11 *Sodium Peroxide* — solid.

56.3.12 *Potassium Hydroxide-Potassium Sulphide Wash Solution* — Dilute 100 ml of the above solution to one litre.

56.3.13 *Concentrated Hydrochloric Acid* — *see* **5.3.3**.

56.3.14 *Hydrogen Sulphide Wash Solution* — Saturate dilute hydrochloric acid (1 : 99) with hydrogen sulphide gas.

56.3.15 *Potassium Chlorate* — solid.

56.3.16 *Oxalic Acid* — solid.

56.3.17 *Hydrogen Sulphide — Oxalic Acid Wash Solution* — Saturate dilute sulphuric acid (1 : 99) with hydrogen sulphide and dissolve in the solution a few crystals of oxalic acid for each 100 ml.

56.3.18 *Ferric Sulphate Solution* — 10 g/l.

56.3.19 *Dilute Hydrochloric Acid* — 1 : 1 (*v*/*v*).

56.3.20 *Test Lead*

56.3.21 *Sodium Bicarbonate Solution* — saturated.

56.3.22 *Starch Solution* — Make a suspension of one gram of soluble starch in about 10 ml of water and add it carefully to 100 ml of boiling water. Boil for two or three minutes and cool. Prepare fresh as needed.

56.3.23 *Potassium Iodide* — solid.

56.3.24 *Standard Potassium Iodate Solution* — 0·03 N. Dissolve 1·20 g of recrystallised potassium iodate in 200 ml of water containing one gram of sodium hydroxide and add 10 g of potassium iodide. When solution is complete dilute to one litre in a volumetric flask. To standardize, dissolve 0·02 g of tin in hydrochloric acid, reduce the tin with test lead and titrate with potassium iodate solution as described under **56.4.5**.

56.4 Procedure

56.4.1 Transfer 5 g of the sample to a platinum dish provided with a cover and add 50 ml of concentrated nitric acid. Add hydrofluoric acid, a little at a time, with occasional heating, until the alloy is dissolved. Evaporate to approximately 25 ml, add 35 ml of concentrated sulphuric acid and continue the evaporation to dense white fumes. Cool and transfer to a 600-ml beaker rinsing the dish successively with dilute ammonium hydroxide and hot dilute sulphuric acid and finally with water. Dilute to about 400 ml, add 20 g of tartaric acid and an excess of concentrated ammonium hydroxide. Heat just short of boiling for several minutes, acidify with concentrated sulphuric acid, adding an excess of 2 ml for every 100 ml of solution and pass a brisk stream of hydrogen sulphide gas at least 30 minutes. Filter and wash with tartaric acid wash solution.

56.4.2 Return the paper and sulphides to the beaker in which the precipitation was made and add 50 ml of potassium hydroxide-potassium sulphide solution and one gram of sodium peroxide. Gradually heat to boiling with occasional stirring, dilute with an equal volume of water, filter into a 400-ml beaker and wash with potassium hydroxide-potassium sulphide wash solution. Discard the residue.

56.4.3 Add concentrated hydrochloric acid to the filtrate until the solution is acidic and then one millilitre in excess for every 100 ml of solution. Filter the sulphides and wash with hydrogen sulphide wash solution. Transfer the paper and precipitate to a 400-ml beaker, treat with 10 ml of concentrated hydrochloric acid and add potassium chlorate, a few crystals at a time, while warming the solution to 40°C. Dilute to 200 ml and boil gently to expel chlorine. Add 5 g of oxalic acid, heat to 70°C and pass in a rapid stream of hydrogen sulphide gas for 20 to 30 minutes. Filter and wash thoroughly with hydrogen sulphide-oxalic acid wash solution. Preserve the filter paper and the precipitate for the determination of antimony.

56.4.4 Add 5 ml of concentrated sulphuric acid to the filtrate and evaporate to dense white fumes. Cool somewhat and dilute with 100 ml of water. Add 50 ml of ferric sulphate solution and heat to boiling. Add dilute ammonium hydroxide till the solution is alkaline, then add 5 ml in excess. Let the precipitate settle, filter and wash with hot water.

56.4.5 Dissolve the precipitate in 80 ml of hot dilute hydrochloric acid (1 : 1) and wash the filter with hot water collecting the solution in a 500-ml Erlenmeyer flask. Add one to two grams of test lead and close the flask with a one-holed rubber stopper carrying a bent delivery tube as shown in Fig. 5. Boil gently on a hot-plate for 20 minutes. At the end of this period immerse the delivery tube in a small beaker containing saturated sodium bicarbonate solution. Remove the flask from the hot-plate and keeping the delivery tube immersed in sodium bicarbonate, allow to cool to room temperature. Remove the stopper, add 5 ml of starch solution, 2 to 3 g of potassium iodide and titrate with standard potassium iodate solution to a permanent blue colour.

56.4.6 Make a blank determination following the same procedure and using the same amounts of reagents, but without the material.

56.5 Calculation

$$\text{Tin, percent} = \frac{(A - B)\,C}{D} \times 100$$

where

A = volume in ml of the standard potassium iodate solution required for the sample,

B = volume in ml of the standard potassium iodate solution required for the blank,

C = tin equivalent of potassium iodate solution in g/ml, and

D = weight in g of the sample taken.

57. DETERMINATION OF ANTIMONY BY THE GRAVIMETRIC METHOD

57.1 Outline of the Method — The precipitate reserved under **56.4.3** is dissolved by means of hydrochloric acid and bromine. Iron and antimony are co-precipitated, dissolved in hydrochloric acid in presence of tartaric acid. Iron is reduced by ammonium bisulphite and antimony precipitated from the acid solution as sulphide. It is ignited to constant weight and weighed as Sb_2O_4.

57.2 Reagents

57.2.1 *Dilute Hydrochloric Acid* — 1 : 3 and 1 : 9 (*v*/*v*).

57.2.2 *Bromine* — liquid.

57.2.3 *Ferrous Sulphate* — solid.

57.2.4 *Potassium Chloride* — solid.

57.2.5 *Concentrated Hydrochloric Acid* — *see* **5.3.3.**

57.2.6 *Concentrated Nitric Acid* — *see* **6.3.1.**

57.2.7 *Dilute Ammonium Hydroxide* — 1 : 1 (*v*/*v*).

57.2.8 *Tartaric Acid* — solid.

57.2.9 *Ammonium Bisulphite Solution* — 200 g/l.

57.2.10 *Hydrogen Sulphide* — gas.

57.2.11 *Hydrogen Sulphide Wash Solution* — Saturate dilute hydrochloric acid (1 : 99) with hydrogen sulphide.

57.2.12 *Ethyl Alcohol*

57.2.13 *Ether*

57.2.14 *Carbon Disulphide*

57.3 Procedure

57.3.1 Dissolve the precipitate reserved in accordance with **56.4.3** in dilute hydrochloric acid (1 : 9) containing few drops of bromine, keeping the volume down to 25 ml. Evaporate the solution to about 5 ml on a steam bath, add one gram of ferrous sulphate, 0·5 g of potassium chloride and 40 ml of concentrated hydrochloric acid. Evaporate the solution again on a steam bath to 5 ml, dilute with 10 ml water, add one millilitre of concentrated nitric acid and heat until the iron is oxidized. Dilute to 100 ml, heat to boiling, add dilute ammonium hydroxide in slight excess, let the precipitate settle, filter off and wash with warm water.

57.3.2 Dissolve the precipitate in 10 to 15 ml of hot dilute hydrochloric acid (1 : 3) containing 0·1 g of tartaric acid. Dilute to 100 ml, heat and add ammonium bisulphite solution drop by drop to reduce the iron. Boil to expel sulphur dioxide, cool and pass a rapid stream of hydrogen sulphide gas for 15 to 30 minutes. Filter through a weighed Gooch crucible and wash successively with hydrogen sulphide wash solution, alcohol, ether and carbon disulphide. Heat the crucible and precipitate gently, adding one drop of concentrated nitric acid from time to time to oxidize the antimony sulphide. Finally heat at about 600°C to constant weight and weigh as Sb_2O_4.

57.4 Calculation

$$\text{Antimony, percent} = \frac{A \times 79{\cdot}2}{B}$$

where

A = weight in g of the antimony oxide, and
B = weight in g of the sample taken.

58. DETERMINATION OF ARSENIC BY THE HYPOPHOSPHITE (IODIMETRIC) METHOD

58.1 Outline of the Method — The sample is fused with sodium peroxide, the melt extracted with water and tungsten kept in solution by phosphoric acid. Arsenic is reduced by sodium hypophosphite to metallic arsenic, in acid medium, and oxidized by a measured excess of standard iodine solution to pentavalent arsenic. The excess iodine is back-titrated with standard arsenious oxide solution.

58.2 Reagents

58.2.1 *Sodium Peroxide* — solid.

58.2.2 *Sodium Carbonate* — anhydrous.

58.2.3 *Phosphoric Acid* —85 percent.

58.2.4 *Concentrated Hodrochloric Acid — see* **5.3.3.**

58.2.5 *Sodium Hypophosphite* — solid.

58.2.6 *Hydrofluoric Acid* — 40 percent.

58.2.7 *Dilute Hydrochloric Acid* — 1 : 3 (*v*/*v*).

58.2.8 *Ammonium Chloride Solution* — 5 percent.

58.2.9 *Standard Iodine Solution* — 0·01 N. Dissolve 0·025 4 g of iodine and 3 g of potassium iodide in 20 ml water and dilute to 200 ml in a volumetric flask.

58.2.10 *Standard Arsenious Oxide Solution* — 0·01 N. Dissolve 0·099 g of arsenious oxide a few millilitres of sodium hydroxide (20 percent) and dilute to 100 ml with water. Pass a brisk current of carbon dioxide for several minutes and then dilute to 200 ml.

58.2.11 *Starch Solution — see* **56.3.22.**

58.2.12 *Sodium Bicarbonate* — solid, carbonate free.

58.3 Procedure

58.3.1 Transfer 5g of an accurately weighed sample, 10g of dry sodium peroxide and 5 g of sodium carbonate to an iron crucible, mix thoroughly with a glass rod and fuse carefully over a Bunsen flame. Just before completion of the fusion, increase the temperature to bright redness for one minute.

58.3.2 Extract the melt with a mixture of 100 ml of water and 40 ml of phosphoric acid in a flask, and rinse the crucible thoroughly with water. Boil it down to about 50 ml. Cool and add 80 ml of cocentrated hydrochloric acid and 40 ml of water. Add 2 g of sodium hypophosphite, warm to brisk effervescence, avoiding boiling, and add further 2 g of sodium hypophosphite until no further effervescence occurs. Add 10 drops of hydrofluoric acid and 12 g of sodium hypophosphite and boil under reflux for 15 minutes.

58.3.3 Cool, filter off the precipitated arsenic and wash the residue first with 100 ml of dilute hydrochloric acid containing 3 g of sodium hypophosphite, then about seven times with ammonium chloride solution. Discard the filtrate, transfer the residue and filter to an 800-ml tall-form beaker, rinsing with about 50 ml of water.

58.3.4 Add a measured excess of the standard iodine solution, stir, allow to stand for five minutes, then dilute to 250 ml and titrate with arsenious oxide solution to pronounced lightening of iodine colour. Treat with a few millilitres of starch solution and discharge the colouration by adding about 3 ml more of the standard arsenious oxide solution and about 2 g of sodium bicarbonate. With vigorous shaking continuously, back-titrate with standard iodine solution.

58.3.5 Make a blank determination using the same amounts of all reagents, but without the material.

58.4 Calculation

$$\text{Arsenic, percent} = \frac{A - (B + C) \times 0{\cdot}000\,15}{D} \times 100$$

where

A = volume in ml of 0·01 N iodine solution used in the test titration,

B = volume in ml of 0·01 N iodine solution equivalent to the standard arsenious oxide solution used,

C = volume in ml of 0·01 N iodine solution consumed by the blank titration, and

D = weight in g of the sample taken.

59. DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

59.1 Determine phosphorus content of the sample by following the procedure as given under **10.3** with the following modification.

59.1.1 Dissolve 2 g of the sample in 15 ml of concentrated nitric acid and 5 ml of hydrofluoric acid in a platinum dish and when decomposition is complete, add 5 ml of perchloric acid and 20 ml of concentrated sulphuric acid. Evaporate to dense white fumes. Cool, dilute with water, boil and filter. Wash the precipitate with hot water, collect filtrate and washings. Further complete the estimation as under **10.3.2** to **10.4**.

60. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

60.1 Outline of the Method — The sample is dissolved in nitric acid, hydrofluoric acid and the tungsten separated as tungstic acid. The residual tungstic acid from the filtrate is removed by α-benzoinoxime solution in presence of cinchonine and sulphur estimated as usual.

60.2 Reagents — In addition to the reagents given under **9.2**, the following reagents are required.

60.2.1 *Sodium Carbonate* — anhydrous.

60.2.2 *Perchloric Acid* — 70 percent.

60.2.3 *Cinchonine Solution* — Wash the cinchonine with water to remove any sulphate and then dissolve 125 g in one litre of dilute hydrochloric acid (1 : 1).

60.2.4 *α-Benzoinoxime Solution — see* **35.2.2.**

60.2.5 *α-Benzoinoxime Wash Solution — see* **35.2.3.**

60.3 Procedure

60.3.1 Transfer 5 g of the sample to a platinum dish and add 100 ml of concentrated nitric acid followed by hydrofluoric acid, a few drops at a time, and heating till the alloy has dissolved completely. Add one gram of sodium carbonate and 30 ml of perchloric acid, evaporate carefully to a syrupy condition. Cool a little, add 100 ml of boiling water and 5 ml of concentrated hydrochloric acid, digest for 30 minutes at 60 to 70°C and filter. Wash the precipitate of tungstic acid with hot dilute hydrochloric acid. Reject the precipitate.

60.3.2 Dilute the filtrate to 250 to 300 ml with hot water, add 5 ml of cinchonine solution and boil for three to five minutes. Cool to 15 to 20°C, add some ashless paper pulp and 5 to 10 ml of α-benzoinoxime solution, stir well for several minutes and filter. Wash the paper and precipitate 10 to 12 times with cold α-benzoinoxime wash solution. Reject the residue. Further complete the estimation as described under **9.3.2** to **9.4**.

APPENDIX A

COMPOSITION RANGES OF FERRO-ALLOYS

(*Clause* 1.1)

Ferro-Alloys	Constituents, Percent														
	Si	C	P	Mn	S	Al	Cr	N	Mo	Ti	V	W	Sn	As	Sb
Ferrosilicon	15 to 75	0·15 to 1·5	0·05 to 0·15	Nil	0·05 *Max*	1·0 *Max*	—	—	—	—	—	—	—	—	—
Ferrochromium	*10 *Max*	8 *Max*	0·05 *Max*	Nil	0·05 *Max*	Nil	50 to 75	4·00 *Max*	—	—	—	—	—	—	—
Ferromanganese and Speigeleisen	7·0 *Max*	8 *Max*	1·00 *Max*	65** *Min*	0·05 *Max*	Nil	—	—	—	—	—	—	—	—	—
Silicomanganese	16 to 20	2·0 *Max*	0·30 *Max*	65 t0 75	0·03 *Max*	Nil	—	—	—	—	—	—	—	—	—
Ferromolybdenum	1·5 *Max*	0·50 *Max*	Nil	Nil	0·25 *Max*	Nil	—	—	60 *Min*	—	—	—	—	—	—
Ferrophosphorus	Nil	1·0 *Max*	20 to 26	Nil	Nil	Nil	—	—	—	—	—	—	—	—	—
Ferrotitanium	2 to 25	8 *Max*	Nil	Nil	Nil	Up to 30	—	—	—	15 *Min*	—	—	—	—	—
Ferrovanadium	11 *Max*	1·0 *Max*	0·10 *Max*	Nil	0·10 *Max*	1·50 *Max*	—	—	—	—	35 *Min*	—	—	—	—
Ferrotungsten	1·0 *Max*	1·0 *Max*	0·06 *Max*	0·80 *Max*	0·06 *Max*	—	—	—	—	—	—	70 *Min*	†0·10 *Max*	†0·08 *Max*	†0·10 *Max*

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*In foundry-grade ferrochromium, silicon may be 28 to 32 percent.

**In speigeleisen, manganese content may be 15 to 25 percent.

†Total of Sn, As and Sb should not be more than 0·2 percent.

Note 1—For small changes in the ranges of constituents which might be made in the relevant Indian Standard Specifications, no change in the method for determination of these constituents will be required.

Note 2—The word 'NIL', wherever it appears in the above Appendix, implies that the constituent has not been specified in the relevant Indian Standard specifications.